THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 3 DECEMBER, 1935 NUMBER 12

Ultraviolet Absorption of Mixtures of NO, NO_2 and H_2O

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(Received August 16, 1935)

In considerable amounts of NO containing small amounts of NO_2 a continuous absorption occurs in the ultraviolet, obscuring both the absorption of NO and that portion of the absorption of NO_2 which lies below 2500A. The behavior of this absorption with respect to temperature and the partial pressures of the constituents is rather convincing evidence that it is due to N_2O_3. When very small amounts of water are also present a group of bands occurs in the near ultraviolet, lying in the same region but not resembling the longer wave-length NO_2 absorption. These bands appear diffuse under low dispersion but possess an ordered arrangement. With increase of temperature the intensity of the bands decreases rapidly. They begin in the vicinity of 3850A, extending to shorter wave-lengths. The first members are broader and more diffuse than those that follow, indicating a predissociation process in the carrier, which is probably HONO.

WHEN the absorption spectrum of pure nitric oxide is photographed in moderate path lengths at atmospheric pressure and room temperature with quartz and ordinary unsensitized plates, the entire spectrum consists of the 0−0 band of the γ system with perhaps the 0−1 band also showing at the extreme short wave-length limit. If a very small amount of oxygen or of nitrogen dioxide be present, however, a continuous absorption overlies this region of the NO bands, which is due to the molecule N_2O_3. If, in addition, a very small amount of water vapor be present, a series of bands appears in the region 4000–3000A which are not characteristic of the NO_2 spectrum, nor, of course, of that of NO. The authors have earlier reported[1] discovering these absorptions during work on the optical dissociation of N_2O, and at that time erroneously attributed the bands also to the carrier N_2O_3. The presence of water vapor as well as both the other constituents is necessary for the production of the bands. A probable carrier of the bands would seem to be the molecule HONO, though a polymer of this molecule would also be a possibility. In this paper they will be referred to as due to HONO, or, as is more often written, HNO_2.

The absorption bands are shown as the two lower portions of Fig. 1, with the absorption of NO_2 above for comparison. Though the positions of such diffuse bands can hardly be given wave-length values with useful accuracy, these bands nevertheless suggest that they comprise two progressions, as is diagrammatically illustrated below the absorption in the figure. The bands set in remarkably close to the position of the first predissociation process in NO_2. The first bands are very diffuse, sharpening noticeably as they proceed to shorter wave-lengths.

If these bands are due to HONO, or a polymer of this, they should show a dependence upon the pressures of the three constituents NO, NO_2 and H_2O, and probably upon the temperature of the mixture, depending upon the magnitude of the

[1] Melvin and Wulf, Phys. Rev. **38**, 2294 (1931).

heat of dissociation of HONO. The continuous absorption due to N_2O_3 should similarly show a dependence upon the pressures of NO and NO_2, and also upon the temperature of the mixture, this latter following from the fact that the heat of dissociation of N_2O_3 into NO and NO_2 has been found to be about 10,300 calories.[2] All of these conditions are fulfilled.

In Fig. 2 the upper picture shows these absorptions at three different partial pressures of NO_2 in a 40-cm path length and constant partial pressure of H_2O and NO, the first strip being the light source through the empty cell, the next lower being taken with H_2O at a pressure of 16 mm Hg and NO at roughly 544 mm Hg (this amount of NO is so great that the $v''=1\rightarrow v'=0$ band shows in absorption at the short wave-length end, even at room temperature). The last three strips show the absorption for approximately 0.5 mm, 1.5 mm and 4.5 mm Hg pressure, respectively, of added NO_2. The lower picture in Fig. 2 is similar, showing the light source through the empty cell, through the cell containing 7.4 mm of NO_2, and thirdly with 5.2 mm of H_2O added, while in the three lower strips NO was added to the cell in three increasing amounts, roughly 35 mm, 215 mm, and 760 mm Hg, respectively.

In Fig. 3 the upper picture shows in a similar way the influence of water vapor, the first strip being the source through the empty cell, the second with the cell containing approximately 7.4 mm of NO_2 and the third with 470 mm of added NO. The three following strips were taken after the addition of water vapor in amounts roughly 0.9 mm, 6.1 mm, and an amount which would have given 41.5 mm Hg had not some undoubtedly condensed out on the walls. In the lower picture of Fig. 3 these absorptions are shown at three different temperatures, the NO_2 pressure being 1.5 mm Hg, the NO pressure 380 mm Hg, and the H_2O pressure 20 mm Hg.

It should be stated that the introduction of the gases into the absorption cell always involved condensing out in a small U-tube, contained in the circulating system which was in series with the absorption cell. This means that the solid and liquid phases were always present, for a short time at least, prior to the above exposures. An all-glass magnetic piston-type pump effected the circulation and resultant mixing. The various amounts of gas added to the cell are given above as pressures they would have exerted had they been alone in the absorption tube system.

There is a further observation which lends weight to the point of view that the bands are due to HNO_2. If, to a cell containing a small amount of NO_2, water vapor be added in excess of saturation until a small amount of liquid water must exist as a film on the walls, the NO_2 may be reduced to a value so low that it cannot be seen. This is probably due to the formation of HNO_3 and NO, the NO making its appearance in absorption. If now NO be added in excess the HNO_2 bands become plain, the NO effecting an increase in the concentration of the HNO_2 which may be many fold, depending upon the degree of dissociation of the HNO_2 prior to the addition.

Certain of the bands give the impression of being related to the NO_2 absorption, because of the close correspondence of their positions with some of the NO_2 bands. However, in the case of such diffuse bands and such relatively low dispersion this may well be fortuitous.[3]

Discussion

At least two suggestions might be made as to the significance of the two groups of bands. They might be thought of as transitions in but one degree of oscillational freedom for which $v''=0$ and $v''=1$. This does not seem probable, however, because the relative intensities of the two progressions to be expected on such a basis do not seem to exist. With increasing temperature the intensity of both progressions decreases rapidly as would be expected owing to the decrease in the concentration of the HONO through thermal dissociation. There is, however, no noticeable tendency for the weaker progres-

[2] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

[3] If this were a real correspondence one might ascribe the bands to a selective enhancement of certain of the NO_2 bands by the mutual action of NO and H_2O. It seems, however, that such an explanation would not differ greatly from attributing the bands to HNO_2 or a polymer thereof.

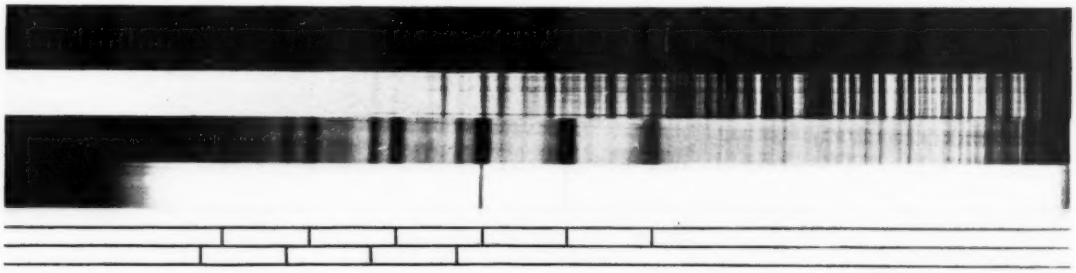

FIG. 1. Absorption bands occurring in mixtures of NO, NO_2 and H_2O, probably due to HNO_2. The absorption of NO_2 is shown above.

FIG. 2*A*. The effect of increasing nitrogen dioxide, showing at left the continuous absorption of N_2O_3, and at the right the absorption bands of HNO_2.

FIG. 2*B*. Similarly, the effect of nitric oxide.

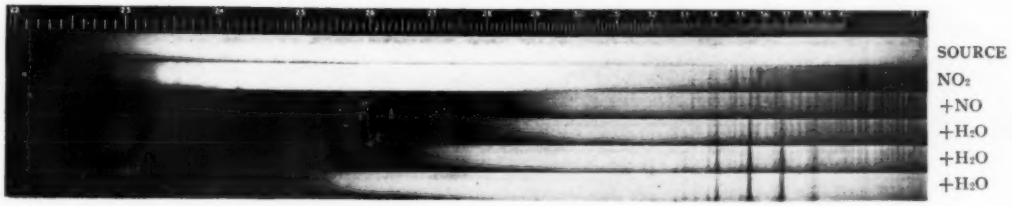

FIG. 3*A*. The effect of increasing water, showing the decrease of the N_2O_3 absorption, and the increase of that of HNO_2.

FIG. 3*B*. Effect of increasing temperature, showing the disappearance of N_2O_3 and HNO_2, and the appearance of NO and NO_2.

sion of the bands to decrease less rapidly than the other progression, which on the interpretation mentioned at the head of this paragraph would be brought about due to the partial offsetting of the decrease in the concentration of the carrier by the increase in the Boltzmann quota of molecules in the vibrational level $v''=1$. If the bands did represent two progressions for which $v''=0$ and $v''=1$, then a minimum value for the initial separation of the levels in this fundamental frequency would be roughly 750 cm^{-1}. Now one may compare the change in the ratio of the numbers of molecules in the zeroth and first vibrational states at 298°K and 473°K with the relative intensity of the bands at these two temperatures. Assuming equal statistical weights, this frequency separation leads to a ratio of populations in the two states at room temperature of roughly 0.027, while at the higher temperature it is about 0.103. This change in relative intensity of only 4-fold might, however, be present in such a mixture of absorptions without being noticeable. However, the ratio of intensities to be expected at room temperature, namely, about 40-fold, also hardly seems to be substantiated in fact, though in the absence of quantitative photometric measurements it cannot be ruled out. It is perhaps doubtful if even the latter would be very conclusive in this mixture of absorptions, and with the NO_2 absorption itself changing somewhat with the temperature.

TABLE I. *Absorption bands of HNO_2.*

WAVE-LENGTH (A)	WAVE NUMBER (cm^{-1})	DIFFERENCES (cm^{-1})
3843	26014	
3681	27159	
3539	28248	
		234
3510	28482	
		784
3416	29266	
		241
3388	29507	
		723
3307	30230	
		268
3278	30498	
		704
3204	31202	
		265
3177	31467	

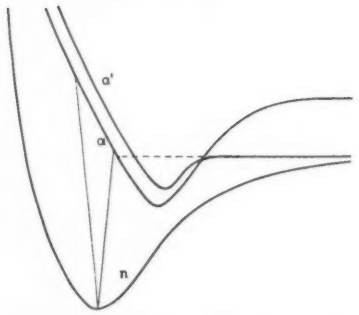

FIG. 4. Diagrammatic potential energy curves.

An alternative hypothesis seems in better accord with the observations, namely, that the transitions all originate from the same normal level and go to several levels in one mode of oscillation in the excited state and to two levels in a second mode of oscillation in the excited state, thus yielding the two partial progressions. From Fig. 1 it can be seen that, on the basis of the first hypothesis, there is the opportunity to obtain three estimates of the separation $v''=1$ to $v''=0$, while on the basis of the second hypothesis there is the opportunity to obtain four estimates of the separation $v_2'=1$ to $v_2'=0$. Table I gives the data for these bands and these two sets of differences. In this comparison lies also a slight indication in favor of the second hypothesis, since in the case of the first estimate, instead of being constant the three observed values decrease progressively, being 784 cm^{-1}, 723 cm^{-1}, and 704 cm^{-1}, respectively, while in the second case the four observed differences are 234 cm^{-1}, 241 cm^{-1}, 268 cm^{-1} and 265 cm^{-1}. The failure of the former to show constancy argues against the first hypothesis, and everything considered the second seems the more probable. The authors obtained similar results in a study of the effect of temperature upon the absorption bands of ozone.[4] In this case the bands are very numerous, and several levels of at least two modes of vibration in the excited state are evident. In spite of this no bands were observed which came from levels of the normal state appreciably higher than the lowest. Since this work, Chalonge and Lefebvre,[5] working with

[4] Wulf and Melvin, Phys. Rev. **38**, 330 (1931).
[5] Chalonge and Lefebvre, Comptes rendus **197**, 444 (1933); ibid. **199**, 456 (1934).

very large effective paths of ozone, have found bands at longer wave-lengths which come from higher vibrational levels in the normal state.

The beginning of the HONO bands so nearly at the point of the first predissociation of NO_2 suggests that there may be a connection between these two phenomena. The exceptional diffuseness of the first bands indicates that at about this energy there exist discrete vibrational states of an electronic level in HONO from which there is a high probability of transition into another electronic level in the molecule, in which, for this energy, the molecule is dissociated, whereas for vibrational states higher than these the probability of transition into this second level grows less. Fig. 4 shows diagrammatically one arrangement of levels in the molecule that could lead to such circumstances,[6] pictured as if but one of the fundamental frequencies of this polyatomic molecule were excited, that is, as if one were dealing with a diatomic molecule.

Franck, Sponer and Teller[7] have discussed predissociation in polyatomic molecules and have explained important differences from the behavior of diatomic molecules that may in general arise. Gradual setting-in of predissociation is one of the important differences. In diatomic molecules it is very improbable, to be expected only where the potential curve of the upper level and the perturbing level intersect in an extremely acute angle. In polyatomic molecules, however, where the relative positions of the atoms are determined by three or more parameters, factors arise in the complicated motion of oscillation which can lead to a gradual setting-in of predissociation, and here it is frequently encountered. But the present case, in contrast, shows a gradual decrease of diffuseness as one passes to higher v' levels. This behavior is in general less to be expected in polyatomic molecules. It becomes possible, however, if the excitation is chiefly in one degree of freedom, and this, indeed, seems to be true in the present case.

The experimental observation that the bands, starting very diffuse, become sharper with increasing frequency seems to be quite certain. It is to be noted that both the increasing dispersion and, for the first few bands also the increasing intensity, act to minimize the appearance of this effect; it is, however, quite apparent in spite of these. This appears to be one of the simplest and most apparent cases of this phenomenon. How far this sharpening of the bands, after the first few, is continued, cannot be said, for they rapidly become faint and are lost in the continuous absorption of N_2O_3.

There are difficulties in the way of obtaining the bands more intensely. Temperature change is of little help, an increase decomposing the HONO, and a decrease reducing its concentration through the reversion of NO_2 to N_2O_4 and the decrease in the saturation pressure of water. Increasing the absolute amount of NO_2 obscures the region by its own absorption. The factor which promises a decidedly favorable change is the pressure of NO. If this could be raised considerably above one atmosphere, an appreciable gain in the concentration of HONO molecules would be expected.

It would be pertinent to raise the question as to the N_2O_3 content of "pure NO_2," for in a mixture of as pure $NO_2 \rightleftharpoons N_2O_4$ as one can prepare there exists the equilibrium $2NO_2 = N_2O_3 + \frac{1}{2}O_2$. Using the free energy value given by Verhoek and Daniels[2] for the reaction $NO_2 + NO = N_2O_3$, $\Delta F_{298^\circ} = +441$ calories, and that given in the *International Critical Tables*[8] for the reaction $NO_2 = NO + \frac{1}{2}O_2$, $\Delta F_{298^\circ} = +8374$ calories, one immediately sees that at room temperature this amount of N_2O_3 will be very small. For NO_2 pressures of a few millimeters the partial pressure of N_2O_3 is of the order of 10^{-5} that of NO_2.

It is interesting that, in the path lengths we have used, the absorption in the red or orange that leads to the blue color of liquid N_2O_3 has not yet been observed. It may be that longer paths will show it. It may also be that this absorption is due to a higher association product such as N_4O_6, appearing with appreciable strengths only at high densities as in the liquid.

[6] Franck and Sponer, Nachr. d. Gesell. d. Wiss. zu Göttingen, p. 241 (1928).

[7] Franck, Sponer and Teller, Zeits. f. physik. Chemie B18, 88 (1932).

[8] *International Critical Tables*, Vol. 7, p. 239.

The Raman Spectra of the Isotopic Molecules H_2, HD, and D_2

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(Received August 29, 1935)

The Raman spectra of H_2, HD and D_2 gases, at 3 atmospheres pressure, were excited by Hg 2537 and photographed with a high dispersion quartz prism spectrograph. A total of 42 lines were analyzed. The positions of the pure rotation lines for H_2 agree with the measurements of Rasetti but the lines in the Q vibration band do not. New vibrational constants calculated from the Raman and emission spectrum data of H_2 and HD give calculated values of the positions of the rotational-vibration Raman lines in good agreement with the values observed for the three isotopic molecules. Contrary to the theoretical predictions, the 0,0 line of the Q vibrational band of HD was observed. A source of error in Raman measurements, namely, the movement of the spectrum due to variations of the barometric pressure during the exposure of a plate, was detected and eliminated.

INTRODUCTION

THE large mass ratios and low moments of inertia of the three hydrogen molecules H_2, HD, and D_2 make them particularly suited for a demonstration of isotopic effects expected in the Raman spectra of diatomic molecules. Several years ago the Raman spectrum of the H_2 molecule was investigated by Rasetti,[1] who succeeded in photographing lines in the pure rotational and the 0–1 rotation-vibration bands. Observation of two rotational lines and the unresolved Q vibrational branch of D_2 was recently reported in a note by Anderson and Yost.[2] In this paper we wish to report measurements of lines in the pure rotation and the 0–1 rotation-vibration bands of the H_2, HD, and D_2 molecules.

In the course of this work, a serious difficulty was encountered, namely, a shift in the spectrum due to fluctuations in the barometric pressure. Merton,[3] working in the visible with a high dispersion glass spectrograph, appears to be the only one to have reported this effect. Although we have found it a serious source of error in Raman measurements, especially for gases where the exposure times are longest, a search has revealed no previous mention of it in the literature on the Raman effect. For this reason we report it in rather greater detail than might otherwise seem necessary.

[1] F. Rasetti, Phys. Rev. **34**, 369 (1929).
[2] T. F. Anderson and D. M. Yost, J. Chem. Phys. **3**, 243 (1935).
[3] T. R. Merton, Proc. Roy. Soc. **A113**, 704 (1926).

EXPERIMENTAL

The first photographs of the Raman spectrum of hydrogen, taken in the region 2450 to 2850A with a Hilger E-1 quartz prism spectrograph, were entirely unsatisfactory for the measurement of the Raman displacements. The lines on two of the plates appeared to be incompletely resolved doublets and on others they appeared diffuse and the rotational structure of the vibrational branch was incompletely resolved. This loss of resolution was found to be due to fluctuations in the barometric pressure during the exposures. Such fluctuations are accompanied by changes in the refractive index of the air in contact with the prism and by consequent changes in the path of the light entering and emerging from it. By photographing the iron arc spectrum through adjacent holes of a Hartmann diaphragm, it was found that shifts of the order of 0.1A frequently occurred during the three hours between successive exposures. Measured values of the shift observed in this way agreed closely with those calculated from the change of the index of refraction of the air with pressure. The shifts were too large to be accounted for on the basis of a pressure effect on the frequency of the lines emitted by the iron arc.

To eliminate the above difficulty, the spectrograph was encased in a pressure-tight steel box having removable ends of aluminum. A crystal quartz window admitted the light to be analyzed. A rack and pinion device was provided for changing the position of the Hartmann diaphragm without opening the box. The instrument was barostatted at 739 mm by use of a mercury

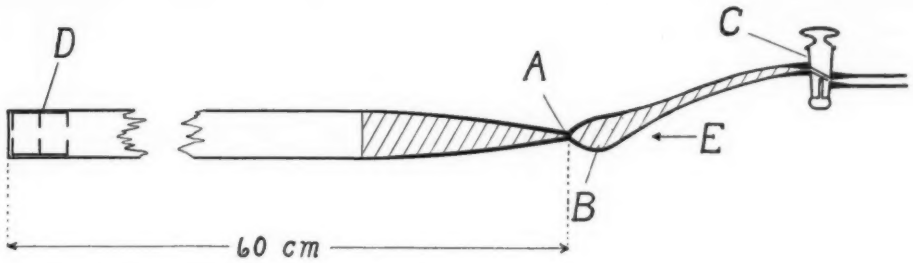

FIG. 1. Raman cell.

manometer contact and a relay controlling a Hyvac oil pump connected to the box. The pressure was maintained constant to within less than 0.1 mm. The instrument was also thermostatted at 32°C to within a few hundredths of a degree.

Subsequent to the barostatting of the spectrograph, additional exposures were made to determine more exactly the magnitude of the pressure effect. During two successive exposures of a plate to the mercury arc, the pressure in the spectrograph was maintained at 595 mm and then at 745 mm. Measurements of the displacement of corresponding lines in the superimposed spectra gave a value of approximately 2.6A/cm change in pressure as compared to the calculated value of 1.7A. The discrepancy between the observed and calculated values is probably to be attributed to the approximate character of the calculations and to strains set up in the spectrograph mounting.

The fused quartz cell in which the gas under study was placed was constructed as indicated in Fig. 1. It was approximately 60 cm long and had an inside diameter of 2.5 cm. The walls of the cell, which were approximately 2 mm thick, were calculated to withstand, with a safety factor of three, two atmospheres in excess of the atmospheric pressure. One end was drawn down symmetrically along the axis of the cell to the 1 mm (I.D.) constriction *A*, to which the subsidiary light horn *B* was added. The Pyrex vacuum stopcock *C* was attached to the cell by means of a seven-step seal. The gas contained in the cell was illuminated by three low pressure Hanovia 2537 Mercury Arcs, the radiating elements of which were quartz tubes (1 cm in diameter and 133 cm long) bent into the shape of closed S's. The arcs were held firmly against the Raman tube by a polished aluminum reflector which was bound around them. Each arc was supplied approximately 100 milliamperes by individual high voltage (0.5 kva) transformers. The arcs maintain a low temperature and therefore were sufficiently cooled by the use of two fans.

The illumination of the spectrograph slit by light coming directly from the walls of the quartz cell was minimized by a series of three platinum diaphragms *D* spun and spot-welded into a platinum sleeve and blackened by the electrodeposition of a thin film of platinum by the method of Lorch.[4] The diaphragms allowed uniform illumination of a 3-mm length of the slit when the tube was placed about three centimeters from it. The cell was easily and accurately aligned along the optical axis of the spectrograph by sighting through a temporarily unblackened portion *E* of the subsidiary light horn and through the constriction *A* and the diaphragms *D* at light sent through the spectrograph in the reverse direction.

The mercury arcs were found to produce high concentrations of ozone resulting in the absorption of λ2537 and also the scattered light. In order to reduce this loss of light, a moderate stream of nitrogen was allowed to flow between the cell and the reflector. It is estimated that this method of eliminating the envelope of ozone around the cell decreased the exposure time by a half or two-thirds. The actual exposure times were from 100 to 200 hours.

The exciting line that was scattered without change of wave-length was partially absorbed by

[4] A. Lorch, Thesis, Columbia University, 1932.

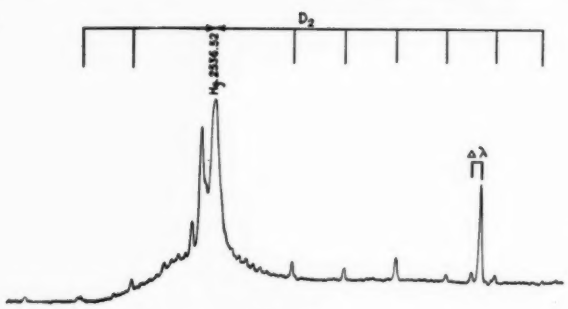

FIG. 2.

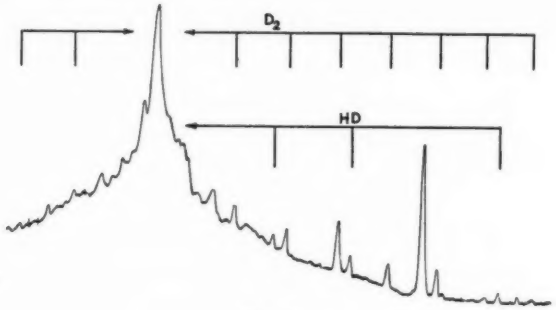

FIG. 3.

vapor from a small quantity of mercury placed in the spectrograph.

The deuterium content of the gas samples used for obtaining Plates I, II, and III was 99, 70, and 60 percent, respectively.

The iron arc was used as a reference spectrum.

RESULTS

In Figs. 2 and 3 are shown the microphotometer curves of the pure rotational spectra on Plates I and II. Plates I and III were taken after the spectrograph was barostatted. Due to the failure of the relay controlling the pump connected to the barostat, the pressure in the spectrograph was reduced from 739 mm to about 600 mm for approximately 10 to 12 hours during the exposure of Plate I. The resultant pressure shift of one of the mercury lines is indicated in the microphotometer curve of Fig. 2 as an apparent change in wave-length $\Delta\lambda$. Plate II is the only one satisfactory for measurement obtained previous to the barostatting of the spectrograph. Even for this plate, however, the line width was somewhat greater than obtains when the pressure is controlled, as may be seen by comparing the curves of Plates I and II in Figs. 2 and 3, respectively.

While photographing the iron spectrum on Plate I an accidental jarring of the spectrograph caused a movement of the plate and resulted in a shift of the reference spectrum with respect to the Raman spectrum. In determining the frequencies of the Raman lines, allowance for this shift was made by determining its value for the Rayleigh scattered mercury lines. It was considered best to obtain the apparent frequency of the irradiating mercury line from the Stokes and anti-Stokes Raman lines on each plate, the values 39,411.9 cm^{-1}, 39,412.43 cm^{-1} and 39,412.35 cm^{-1} being found for Plates I, II, and III, respectively.

The error in measurement of the lines varies from 0.5 to 1.0 cm^{-1} except for several very weak lines. It is estimated that the average values of the three plates are good to approximately 0.3 cm^{-1}.

In order to calculate the frequencies, the following expression for the energy[5] was used:

$$E/hc=\tilde{\omega}_e(v+\tfrac{1}{2})-x\tilde{\omega}_e(v+\tfrac{1}{2})^2 +y\tilde{\omega}_e(v+\tfrac{1}{2})^3-z\tilde{\omega}_e(v+\tfrac{1}{2})^4 +[B_e-\alpha_e(v+\tfrac{1}{2})+\gamma_e(v+\tfrac{1}{2})^2-\delta_e(v+\tfrac{1}{2})^3]J(J+1) +[D_e+\beta_e(v+\tfrac{1}{2})]J^2(J+1)^2+F_eJ^3(J+1)^3:$$

The constants used are those of Jeppesen[6, 7] as recalculated by Urey and Teal.[8] Below is given, in Tables I and II, a comparison of the calculated and observed values of the frequencies in wave numbers in vacuum.

It will be seen in Table I that there is good agreement between the observed and calculated values of the pure rotational lines. Though a trend in the values for D_2 indicates that the rotational levels for this molecule may be closer together than predicted by theory the variation from the theoretical values is within the experimental error for most lines. Very good agreement is had between the values for H_2 in Table I and those found by Rasetti[1] and Bhagavantam.[9] For

[5] W. Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge (1932).
[6] C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).
[7] C. R. Jeppesen, Phys. Rev. **45**, 480 (1934).
[8] H. C. Urey and G. K. Teal, Rev. Mod. Phys. **3**, 243 (1935).
[9] S. Bhagavantam, Ind. J. Phys. **6**, 319 (1931); **7**, 105 (1932).

TABLE I.

	v	J	PLATE I	PLATE II	PLATE III	AVERAGE	CALC.	DIFFERENCE
H_2	0–0	3–1	—	—	586.3	586.3	587.0	−0.7
		2–0	—	—	354.3	354.3	354.3	0.0
		0–2	—	—	354.5	354.5	354.3	+0.2
		1–3	—	587.1	586.9	586.9	586.9	0.0
		2–4	—	—	815.3	815.3	814.4	+0.9
		3–5	—	—	1034.5	1034.5	1034.5	−0.1
HD	0–0	4–2	—	—	616.0	616.0	616.2	−0.2
		3–1	—	444.2	442.5	443.3	443.1	+0.2
		2–0	—	—	268.0	268.0	267.1	+0.9
		0–2	—	267.9	266.4	267.1	267.1	0.0
		1–3	—	443.0	442.9	443.0	443.1	−0.1
		2–4	—	—	616.0	616.0	616.2	−0.2
		3–5	—	785.4	784.5	784.9	785.2	−0.3
		4–6	—	—	949.3	949.3	949.1	+0.2
D_2	0–0	6–4	—	—	642.2	642.2	643.5	−1.3
		5–3	—	528.2	530.2	529.2	530.3	−1.1
		4–2	—	416.1	414.2	415.0	414.9	+0.1
		3–1	297.5	297.5	296.4	297.3	297.7	−0.6
		2–0	178.7	178.9	179.3	179.0	179.1	−0.1
		0–2	178.7	179.0	178.7	178.8	179.1	−0.3
		1–3	297.2	298.0	297.1	297.4	297.7	−0.3
		2–4	414.6	415.3	414.5	414.8	414.9	−0.1
		3–5	530.0	530.3	530.1	530.1	530.3	−0.2
		4–6	642.1	642.3	642.4	642.3	643.5	−1.2
		5–7	752.2	752.6	752.9	752.6	754.1	−1.5

the Q vibrational branch of H_2, however, discrepancies appear between the values found in this work and the measurements of Rasetti. The possibility that the differences between these values and Rasetti's might be due to the effect of pressure was considered since Rasetti's observations were made at approximately 12 atmospheres whereas the values in Tables I and II are for gas at 3 atmospheres. Bhagavantam did not observe an effect on the lines of hydrogen when the pressure was varied from 13 to 50 atmospheres, but no previous measurements at lower pressures, as used here, are available.* The cause of the differences is not yet understood. The discrepancies are not cleared up by the measurements of Bhagavantam since these latter values agree in part with the measurements given in Table II and in part with those of Rasetti. Since agreement was had between the measured values obtained from three plates and the discrepancies between the observed and calculated values, given in Table II, were consistent, it was concluded that the vibrational constants were incorrect. New vibrational constants were therefore calculated. Least-square solutions of the ΔG values for the first seven states were obtained for H_2 from the data of Jeppesen,[6] Rasetti[10] and this study and for HD from the data of Jeppesen,[7] Mie[11] and this study. Our experimental values for $\Delta G_{\frac{1}{2}}$ are:

$$\Delta G_{\frac{1}{2}}(H_2) = 4160.2 \pm 0.2 \text{ cm}^{-1},$$
$$\Delta G_{\frac{1}{2}}(HD) = 3631.4 \pm 0.2 \text{ cm}^{-1},$$
$$\Delta G_{\frac{1}{2}}(D_2) = 2993.5 \pm 0.2 \text{ cm}^{-1}.$$

The emission spectrum data and Rasetti's and the present Raman data were weighted 1, 3, and 5, respectively. The best values of the constants thus obtained are listed in Table III. The relationship observed between the ω_e's of H_2 and HD agrees excellently with the theory and the agreement for the $x\omega_e$'s, $y\omega_e$'s, and $z\omega_e$'s, is about as good as could be expected from the accuracy of the data and from the number of levels used in

TABLE II.

	v	J	PLATE I	PLATE II	PLATE III	AVERAGE	CALCULATED U. & T.	CALCULATED T. & M.	DIFFERENCE U. & T.	DIFFERENCE T. & M.
H_2	0–1	0–0	—	—	—	—	4162.4	4160.4	—	—
		1–1	—	—	4154.1	4154.1	4156.5	4154.5	−2.4	−0.4
		2–2	—	—	4143.2	4143.2	4144.6	4142.6	−1.4	+0.6
		3–3	—	—	4124.5	4124.5	4127.2	4125.2	−2.7	−0.7
HD	0–1	0–0	—	—	3630.8	3630.8	3634.2	3631.5	−3.4	−0.7
		1–1	—	3628.8	3627.5	3628.1	3630.5	3627.7	−2.4	+0.4
		2–2	—	3620.0	3619.9	3620.0	3622.8	3619.9	−2.8	+0.1
		3–3	—	3609.6	3608.2	3608.9	3611.3	3608.5	−2.4	+0.4
		4–4	—	3592.8	3592.3	3592.5	3596.1	3593.2	−3.6	−0.7
D_2	0–1	0–0	—	—	—	—	2996.1	2993.2	—	—
		1–1	2992.1	2992.1	2992.5	2992.2	2994.0	2991.1	−1.8	+1.1
		2–2	2986.4	2986.0	2987.2	2986.9	2989.7	2986.9	−2.8	0.0
		3–3	2980.8	2979.8	2980.0	2980.1	2983.4	2980.5	−3.3	−0.4
		4–4	2972.6	2971.9	2972.6	2972.4	2975.1	2972.2	−2.7	+0.2
		5–5	—	2963.6	2961.6	2962.3	2964.6	2961.8	−2.3	+0.5
		6–6	—	2948.3	—	2948.3	2952.2	2949.3	−3.9	−1.0
		0–2	—	3167.5	3165.0	3166.3	3168.9	3166.0	−2.6	+0.3
		1–3	—	3278.5	—	3278.5	3281.1	3278.2	−2.6	+0.3
		2–4	—	3385.9	3387.1	3386.5	3390.0	3387.1	−3.5	−0.6

* In this connection it is interesting to note that the nitrogen vibration line appeared on Plate III, and the measured value of its position was less than that recorded by Rasetti for nitrogen at 12 atmospheres by approximately the same amount as observed for the hydrogen lines.

[10] Data of Rasetti as recalculated by R. T. Birge and C. R. Jeppesen, Nature **34**, 463 (1930).

[11] K. Mie, Zeits. f. Physik **91**, 475 (1934).

TABLE III.

	H_2	HD	D_2	ρ'': H_2-HD Obs.	ρ'': H_2-HD Theory
ω_e	4405.30	3817.09	3117.05	0.86648	0.86616
$x\omega_e$	125.325	94.958	63.034	0.7577	0.7502
$y\omega_e$	1.9473	1.4569	0.74526	0.748	0.650
$z\omega_e$	0.11265	0.07665	0.031573	0.680	0.563

calculating these constants.* The molecular constants of D_2 given in the table are the average values calculated from those of H_2 and HD, assuming the theoretical relationships between the reduced masses of H_2 and D_2 and of HD and D_2 to hold. The value of ΔG_1 (D_2) calculated by use of these constants is 2993.2 cm^{-1}, which differs from the experimental value of 2993.5 cm^{-1} by only 0.1 cm^{-1} more than the estimated accuracy of the experimental value. The agreement of the observed positions of the rotational vibration lines of the three isotopic molecules and the positions calculated from the new constants is very good, as may be seen from Table II.

The measurement of the heights of the intensity maxima of the microphotometer curves of Plates I and II shows an alternation of intensities of the pure rotational lines of D_2, the lines involving transitions from even states being more intense. This, in agreement with previous work on emission spectra,[12, 13] allows one to conclude that the deuterium nucleus obeys the Einstein-Bose statistics and has a spin different from zero. The semi-quantitative measurements agree very well with those expected according to Placzek's theory[14] if Murphy and Johnston's value of the spin equal to 1 is used. Though the theory predicts the absence of lines corresponding to V : 0–1, J : 0–0 transitions a line for this transition for HD was observed on Plate III.

ACKNOWLEDGMENT

We wish to express our appreciation to Professor H. C. Urey for advice and encouragement during the course of this investigation. One of us (G.E.M.) wishes to thank Professor Urey for financial assistance from the E. K. Adams Fellowship Fund. We are indebted to Dr. A. Dingwall for helpful suggestions and to the Physics Department for placing a spectrograph at our disposal.

* It seems improbable that the theoretical relationships between the constants of the isotopic molecules could hold exactly due to differences to be expected in the potential energy curves from the differences in the electronic zero-point energies of the hydrogen and deuterium atoms as well as the molecules. This effect, however, should be small and not detectable in the constants in Table III.

[12] G. N. Lewis and M. F. Ashley, Phys. Rev. **43**, 837 (1933).
[13] G. M. Murphy and H. Johnston, Phys. Rev. **46**, 95 (1934).
[14] G. Placzek, *Handbuch der Radiologie VI* (1934), Vol. 2, p. 343.

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

On the Possibility of a Metallic Modification of Hydrogen

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(Received October 14, 1935)

Any lattice in which the hydrogen atoms would be translationally identical (Bravais lattice) would have metallic properties. In the present paper the energy of a body-centered lattice of hydrogen is calculated as a function of the lattice constant. This energy is shown to assume its minimum value for a lattice constant which corresponds to a density many times higher than that of the ordinary, molecular lattice of solid hydrogen. This minimum—though negative—is much higher than that of the molecular form. The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.

(1) Introduction

THE present calculation of the constants of metallic hydrogen has a threefold purpose. First, we wanted to explore the possibility of preparing metallic hydrogen under high pressures.[1] The hope for this, however, appears to be small, as the pressures under which metallic hydrogen would be stable seem to be unattainable with the present techniques. Second, it seemed to us important to check the free electron method of calculating wave functions and heats of vaporization[2] in a case where experiments give an upper limit to the energy. The obvious instability of metallic hydrogen under ordinary pressure shows that its heat of formation is smaller than that of the molecular hydrogen. This condition proved to be only too well fulfilled. Finally, we hoped to obtain some information concerning the conditions for the metallic state and the line separating metals from metalloids in the periodic table.[3] This purpose has been achieved by the present work to the extent expected, but this point, although perhaps apparent to the reader, will not be stressed in the present paper.

(2) Calculation

The calculation itself was a rather mechanical application of the principles outlined elsewhere.[2] First, the energy $E(r_s)$ was found for which the solution of the Schrödinger equation with the ordinary Coulombic potential $-e^2/r$ had zero derivative at distance r_s. This was done by a numerical method and, in addition, checked by an analytic approximation,[4] which gave a direct expression for the wave function needed for subsequent work. The plot (lower curve of Fig. 1) shows the results of the numerical method which gave the more accurate results. Its values lie about 0.02 Ry (Rydberg units) below those of the analytic formula. In this case $E(r_s)$ has no minimum, as in case of Na, but instead continues to fall to $-\infty$ for $r_s \to 0$. In Na the rising of $E(r_s)$ for small r_s results from the energy necessary to press the valence electron into the inner shells, whereas no such shell exists for hydrogen.

The upper curve of Fig. 1 is obtained by adding to $E(r_s)$ the Fermi energy for free electrons,

$$(2.2099/r_s^2)\text{Ry},$$

where r_s is expressed in Bohr units $\hbar^2/e^2m$. This corresponds to the calculation adopted in ref. 2 I and gives a minimum of $E=-1.156$ for $r_s=1.50$. This would give a density of 0.80 (as compared to 0.087 in the solid molecular form!) and a heat of vaporization of 48.7 cal. into atomic hydrogen, as compared with 52.5 cal., the heat of formation of the molecular form. We see that the molecular form is the more stable, even according to this very approximate calculation, but if this were all, it would probably still be possible to transform it under pressure to a metallic form.

Unfortunately, a great number of corrections must be applied to the simple picture given in ref. 2 I which decreases the stability of the metallic form in this instance. These corrections are given for the flat wave functions in refs. 2 II and 2 III. They are:

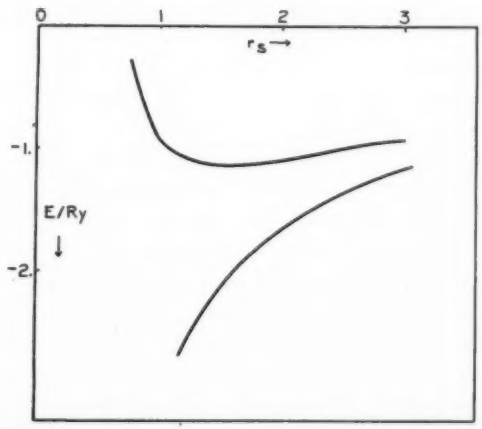

FIG. 1. Lower curve—the energy of the electrons without momentum, the upper curve—total energy as a function of lattice constant. Both according to a naïve free electron theory.

[1] It was J. D. Bernal who first put forward the view that all substances go over under very high pressures into metallic or valence lattices.

[2] (I) E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); (II) **46**, 509, 1934; (III) E. Wigner, ibid. **46**, 1002 (1934); (IV) F. Seitz, ibid. **47**, 400 (1935); (V) J. C. Slater, ibid. **45**, 794 (1934). E. L. Hill remarks in a "Note on the Statistics of Electron Interaction" (Physik. Zeits. Sowjetunion **7**, 447 (1935)) that the expressions "parallel spin" and "antiparallel spin" should be replaced by "parallel spin Z components" and "antiparallel spin Z components," respectively. The former expressions are not quite equivalent with the latter ones according to the general formalism of the statistical interpretation of quantum mechanics and can be used only as an abbreviation for them. (This is done in the present paper also.) We believe that Dr. Hill's further remarks concerning the papers of this reference are based on a misunderstanding.

[3] Interesting quantum-mechanical considerations on this point have been put forward by F. Hund (International Conference on Physics, October 1934, London).

[4] To be given in Section 3.

(a) The difference between the energy of the electron clouds (§2 in II) and the exchange energy (§3 in II)

$$0.284/r_s - 0.017/r_s^2(E_k - E), \quad \text{(in Rydberg units)}, \quad (1)$$

where E_K is a mean value of the energy of the higher s terms and has been estimated[4] to be about 20 Ry/r_s^2. The second term in (1) is, therefore, almost negligible.

(b) The correlation energy, calculated in ref. 2 III, which can be represented for $r_s > 1$ rather closely by

$$-0.584/(r_s + 5.1). \quad (2)$$

(c) A correction for the Madelung number will be added in the next section.

The energy after the corrections (a) and (b) have been added is plotted on a magnified scale on the lowest curve in Fig. 3. One sees that a great part of the binding energy is lost.

(3)

It is very probable that the wave functions have nearly the form $e^{ip\cdot x/\hbar}$, not only in Na, but also in the other alkalies excepting Li.[5] In H this is not the case, however, and there will be further corrections introduced into the energy curve similar to those calculated for Li by F. Seitz.[2 IV] Still the situation for H is rather different from that for Li. In H the wave function of the lowest energy electron ($p=0$) is strongly modulated but the modulation does not increase much for higher p functions. In Li the wave function for $p=0$ was quite flat and the modulation increased with increasing p.

For the calculation of these effects an approximate method has been used. The equation for the wave function of the electron with the momentum p, multiplied by $e^{ip\cdot x/\hbar}$, is[6]

$$H_\mu \chi_\mu = -\Delta\chi_\mu - i\mu\cdot\text{grad}\ \chi_\mu - 2\chi_\mu/r = \epsilon_\mu \chi_\mu, \qquad \mu = 2\hbar p/e^2 m. \quad (3)$$

Here the ϵ_μ does not include the kinetic energy of the flat wave functions, $p^2/2m = \mu^2/4$ Ry. The $\epsilon_\mu - \epsilon_0$ will give us the change in the Fermi energy, and the wave functions χ_μ the change in charge distribution, which are both caused by the fact that the electrons are not free in the lattice. The charge distribution is used in a recalculation of the interaction of the electron clouds and the Fermi hole (exchange energy). We shall see that χ_μ can be assumed to be the sum of a function of r alone (s part) and a function of r multiplied by $(\mu\cdot r)$ (p part). The boundary condition for the χ_μ is periodicity in the lattice, which means zero derivative for the s part, and vanishing of the p part on the surface of the s sphere.

Eq. (3) has been solved by a perturbation method. We shall need only those solutions of the unperturbed equation

$$-\Delta\xi_{nl} = \eta_{nl}\xi_{nl}, \quad (4)$$

which are functions of r alone ($l=0$, or the s part of χ), and those which are functions of r multiplied by $(\mu\cdot r)$, ($l=1$ or the p part of χ). The boundary conditions for these ξ functions are the same as for the corresponding part of χ. We have[2 II]

$$\begin{aligned} &\xi_{00} = (3/4\pi r_s^3)^{\frac{1}{2}}, \quad \xi_{n0} = c_n(\sin\omega_n r)/r, \\ &\xi_{n1} = (3^{\frac{1}{2}}c_n/\mu\omega_n)(\mu\ \text{grad})(\sin\omega_n r)/r, \\ &\eta_{00} = 0, \quad \eta_{n0} = \eta_{n1} = \omega_n^2, \end{aligned} \quad (5)$$

with

$$\omega_1 = \frac{1.430\pi}{r_s}, \quad c_1 = \frac{1.024}{(2\pi r_s)^{\frac{1}{2}}};$$

$$\omega_n = (n+\tfrac{1}{2})\frac{\pi}{r_s}, \quad c_n = \frac{1}{(2\pi r_s)^{\frac{1}{2}}}$$

when the last two expressions hold well for $n>1$ only.

Next we must calculate the matrix elements of H_μ. All terms give nonvanishing elements between ξ_{nl} and $\xi_{n'l}$ only, except for $i\mu\cdot$grad which gives elements between ξ_{nl} and $\xi_{n'l+1}$. We have

$$\begin{aligned} &(H_\mu)_{00;\,00} = -3/r_s; \\ &(H_\mu)_{10;\,10} = 20.2/r_s^2 - 5.65/r_s; \\ &(H_\mu)_{n0;\,n0} \approx (H_\mu)_{n1;\,n1} \approx (n+\tfrac{1}{2})^2\pi^2/r_s^2; \\ &(H_\mu)_{11;\,11} = 20.2/r_s^2 - 3.66/r_s; \\ &(H_\mu)_{n'0;\,n1} = -(i\mu\omega_n/3^{\frac{1}{2}})\delta_{n'n}; \\ &(H_\mu)_{00;\,10} = 1.36/r_s; \\ &(H_\mu)_{00;\,n0} = 2(6)^{\frac{1}{2}}/(n+\tfrac{1}{2})\pi r_s. \end{aligned} \quad (6)$$

[5] Cf. F. Mott and C. Zener, Proc. Camb. Phil. Soc. **30**, 249 (1934); also J. Bardeen and E. Wigner, Phys. Rev. **48**, 84 (1935); for Li see reference 2 (IV) and J. Millman, ibid. **47**, 286 (1935).

[6] Cf. Eq. (11), reference 2 (II). The energy in (3) is in Rydberg units Ry and the length in Bohr units.

For $\mu=0$, this gives, by Rayleigh-Schrödinger formulas,

$$\epsilon_0=\frac{3}{r_s}\frac{(1.36)^2}{20.2-2.65r_s}-\sum_{n=2}^{\infty}\frac{24}{(n+\frac{1}{2})^4\pi^4},$$
$$\chi_0=\xi_{00}+\frac{1.36r_s}{20.2-2.65r_s}\xi_{10}+\sum_{n=2}^{\infty}\frac{2(6)^{\frac{1}{2}}r_s}{(n+\frac{1}{2})^3\pi^3}\xi_{n0}. \quad (7)$$

These are the formulae to which we referred in Section 2. For $\mu\neq 0$, we diagonalized the three rows and columns of H_μ referring to ξ_{00}, ξ_{10} and ξ_{11} and used only for the remaining ones the Rayleigh-Schrödinger method. This was advisable, because $(H_\mu)_{10;\,10}$ and $(H_\mu)_{11;\,11}$ were close together. This gave

$$\epsilon_\mu=\frac{3}{r_s}\frac{1.85}{20.2-2.65r_s-6.72\mu^2(20.2-0.6r_s)^{-1}}-0.0093. \quad (8)$$

The mean value of $\epsilon_\mu-\epsilon_0$ with the weight μ^2, from $\mu=0$ to $\mu=3.84/r_s$ is the correction to the Fermi energy; it is plotted in the lowest curve of Fig. 2. It is negative, just as in Li, because there is no p level below the s level of the valence electron. The energy $\epsilon_\mu-\epsilon_0$ is no longer very accurately proportional to μ^2, because the effect of the next Brillouin zone is appreciable.

(4)

Next the interaction of the electron cloud and the more accurate exchange energy must be derived. The greater density near the nucleus makes it evident that the first will be greater than the free electron value assumed in the previous section. This is true also for the exchange energy, because the Fermi hole is more effective in consequence of the uneven charge distribution. The two effects work against each other, but in contrast to Li, the former is greater here and decreases the binding.

The calculation of these quantities is a little laborious and contains nothing of principal interest. It will be sketched only.

The square of the calculated wave function, i.e., the electric density ρ, was approximated by an analytical expression[7] containing a constant

[7] The reason for this is that only for this form were we able to perform the integrations.

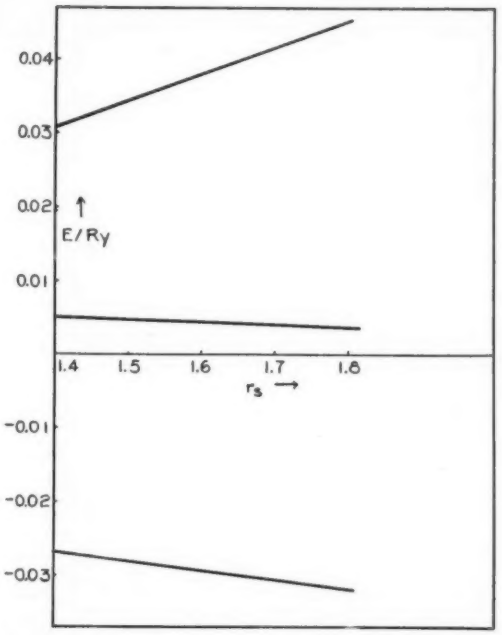

FIG. 2. Bottom line, correction to the Fermi energy; middle line, correction for the Madelung number; top line, correction for the interaction energy.

and an exponentially decreasing charge distribution around each ion:

$$\rho=\rho_1+\rho_2, \quad \rho_1=e(1-c)/(4\pi r_s^3/3). \quad (9)$$

ρ_2 itself contains two parts: first the exponential charge distribution around the ion, in the s sphere in which we are, and second the exponential charge distribution around the other ions. The latter was averaged over all directions so that ρ_2 also became spherically symmetric in each s sphere

$$\rho_2=\frac{ec\beta^3}{8\pi}\left[e^{-\beta r}+4k\frac{\mathrm{Sh}(\beta r)}{\beta r}\right],$$
$$k=e^{-2\beta r_s}(1+\beta r_s+\beta^2 r_s^2/2)(\beta r_s-1)^{-1}. \quad (9a)$$

The two constants c and β were adjusted so as to fit the square of the calculated wave function (7) best.

The potential corresponding to this charge distribution contains also two parts: Φ_1, corresponding to the constant part ρ_1 and Φ_2 corresponding to ρ_2 which could be easily calculated, and hence also the interaction of the electron clouds.

For the calculation of the exchange energy the wave functions of the electrons with momentum p were assumed to be in the form $e^{i(p\cdot x)/\hbar}\chi(r)$ where $\chi(r)$ is the wave function of the lowest state. Under these conditions, the exchange energy is[2 II, 2 III]

$$-\frac{e^2}{2}\int \rho(r)\rho(r')g(|r-r'|)\frac{1}{|r-r'|}dr\,dr', \qquad (10)$$

where

$$g(r)=9\left[\frac{\sin(r/d)-(r/d)\cos(r/d)}{(r/d)^3}\right]^2$$

$$\approx e^{-1.6r/d}\left[1+1.6\left(\frac{r}{d}\right)+1.2\left(\frac{r}{d}\right)^2\right] \qquad (10a)$$

with $d=0.521r_s$. All the integrations could be carried out in elliptic coordinates. The result is evidently a quadratic function in c. The constant term is simply the exchange energy for flat wave functions ($c=0$), i.e., $0.916\text{Ry}/r_s$. The linear terms vanish as may be seen from the following. The integral of the first term in $\rho_1(r)$ times $g(|r-r'|)/|r-r'|$ over r is independent of r'. The product of this quantity and the terms containing c in $\rho(r')$, integrated over r', must vanish, since the integral of $\rho(r')$ is independent of c. By analogy the other linear term vanishes also and the sole remaining correction to the exchange energy of $0.916\text{Ry}/r_s$ goes with c^2. Hence this is a second order effect[8] of the deviation from flatness of the wave function (9), and smaller than the increase of the interaction of the charge clouds which is a first order effect.

Next the change of the correlation energy, due to the uneven charge distribution, has to be considered. In the case of even distribution, the correlation energy is certainly smaller than $0.292e^2/r_s$, even for a very great lattice constant. For the actual uneven distribution in a greatly expanded lattice, however, this energy is as follows. Hartree's equations, solved for many electrons in the field of many ions, give as wave functions of the electrons a sum of spherically symmetric maxima around every ion. If all ions are sufficiently far removed from each other, these waves—let their form be $u(r)$—no longer overlap. The total interaction energy per electron is

$$\tfrac{1}{2}\int \Phi(r)\,|u(r)|^2 4\pi r^2 dr \qquad (11)$$

where $\Phi(r)$ is the potential of the charge distribution $|u(r)|^2$. Since no such interactions actually exist, Hartree's equation gives an incorrect result by this amount, which will be compensated by the exchange and correlation energy.

If Fock's picture is used instead, the interaction energy between electrons with parallel spins vanishes in consequence of the enormously increased Fermi hole. There remains still the interaction between electrons with antiparallel spin, by which amount Fock's picture is still in error. This remaining half of (11) must be nullified by the correlation energy. It follows that this energy must greatly exceed $0.292e^2/r_s$, the largest value possible for flat functions. We see that the correlation energy is increased by the modulation of the waves by a greater factor than the exchange energy, and it becomes in the limiting case of an infinite lattice just one-half of (11), approximately $\frac{1}{4}$Ry per electron.[9]

We have increased the correlation energy for flat waves, given in,[2 III] by the same factor by which the exchange energy appeared to be increased. The total change of the electron interaction energy was positive, and plotted in Fig. 2 also.

Finally, the correction for the Madelung number, as given in appendix 2, Reference[2 II] is given in the same plot. The sum of all three corrections has been added to the curve of Fig. 3 and the upper full line of this figure obtained. This curve assumes its minimum of -1.05Ry (heat of vaporization about 16 Cal.) for $r_s=1.63$ Bohr units, corresponding to a density of 0.62. The possible error in these figures is quite large, because the correction quantities are so great.

(5)

The last quantity which had to be calculated for the thermal constants of metallic H was the zero-point energy corresponding to the half-

[8] This differs from the case for Li.

[9] We emphasize this point since doubts have been raised whether the correlation energy actually exists.

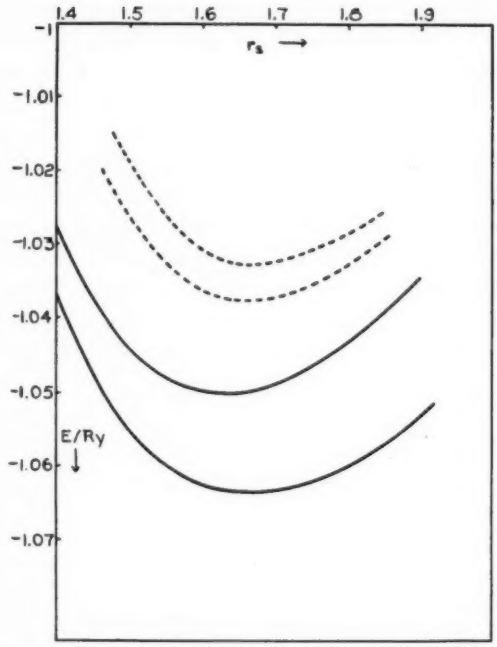

FIG. 3. Energy of the lattice as a function of lattice constant. Lowest curve, for flat wave functions; second curve with all corrections, except zero-point energy of nuclei; the dotted lines contain the zero-point energy, the lower for heavy, the upper for ordinary H.

quanta vibration of the nuclei. If the elastic constants of the medium were known, the elastic spectrum and the zero-point energy could be calculated following Blackman[10] or a paper of Barnes, Brattain, and Seitz.[11] Since, however, only the compressibility can be derived from Fig. 3 (and this only very inaccurately, as it may be in error by as great a factor as two), it was performed by the older method of Debye.[12]

From the curvature of the upper curve in Fig. 3 one obtains for the reciprocal compressibility of a lattice of very heavy hydrogen,

$$\begin{aligned}\tfrac{1}{3}(c_{11}+2c_{12}) &= 2.9\times10^{12}\ \text{dyne/cm}^2 \text{ for } r_s=1.5\\ &= 1.5\times10^{12}\ \text{dyne/cm}^2 \text{ for } r_s=1.6\\ &= 1.1\times10^{12}\ \text{dyne/cm}^2 \text{ for } r_s=1.7\\ &= 0.8\times10^{12}\ \text{dyne/cm}^2 \text{ for } r_s=1.8.\end{aligned}$$

By analogy with other metals $c_{11}=2c_{12}=4c_{44}$ was assumed. The zero-point energy is then about $0.0244(E'')^{\frac{1}{2}}$Ry, where E'' is the second derivative of the energy in Ry with regard to r_s in Bohr units. For the isotropic hydrogen with mass two the value is $0.0173(E'')^{\frac{1}{2}}$Ry. The dotted lines of Fig. 3 give the final results for the lattice energy, the upper one is for light, the lower for heavy hydrogen. The density of the former is 0.59, its heat of formation out of atomic hydrogen 10 Cal. We think that this figure is somewhat too low because the correlation energy is greater than we assumed it to be.

(6) Conclusion

The great density of the hypothetical metallic form of H is not surprising. It seems to be the general rule that the density of the metallic and valence lattice of a substance be greater than that of the layer lattice, and this in turn has greater density than the molecular lattice. Table I illustrates the point.

This table makes it natural to assume that all atoms are bound together by shared electron forces in metallic and valence lattices, and that this is the case also for the atoms within a layer in layer lattices. The different layers are bound together, however, more weakly, perhaps by van der Waals forces. This is well in accord with the general geometric considerations of A. Reis and K. Weissenberg.[13] It seems sensible, therefore, to speak about valence-like forces between two atoms in a lattice, if the density of the outermost electrons of both overlaps considerably at this distance.[14]

The heat of formation of the ordinary, molecular H_2 lattice is 52.5 Cal., practically one-half of the heat of dissociation. Although the figures of the preceding section may be in error by quite a few calories, it is evident that the molecular form is so much more stable (by about 40 Cal.) than the metallic, that the chances of obtaining the latter are extremely small.

In the ordinary lattice, there are two "nearest distances." The distance between two atoms of the same molecule is $0.75\text{A}=1.45a_0$, while the nearest distance between two H atoms of

[10] M. Blackman, Proc. Roy. Soc. London **A148**, 365, 384, (1935); **149**, 117, 126 (1935).
[11] Barnes, Brattain and Seitz, Phys. Rev. **48**, 582 (1935).
[12] Cf. e.g., E. Schrödinger, *Geiger-Scheel Handbuch der Physik*, Vol. X.
[13] A. Reis, Zeits. f. Physik **1**, 204 (1920); **2**, 57 (1920); K. Weissenberg, Zeits. f. Krist. **62**, 12, 52 (1925).
[14] This corresponds also to the ideas developed by L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); J. C. Slater, Phys. Rev. **38**, 1109 (1931).

TABLE I.

SUBSTANCE	DENSITY		DENSITY
As, metallic	5.72	yellow	2.03
Diamond	3.51	graphite	2.24
Black phosphorus	2.70	yellow	1.83
Se, metallic	4.82	red	4.47
Sn, white	7.28	grey	5.76

different H_2 molecules is about $3.3A = 6.3a_0$.[15] If one compresses the ordinary lattice, the latter distance will decrease, the former increase, as follows already from the calculations of F. London.[16] Thus, the increase of the pressure brings the intermolecular distances nearer to the intramolecular distances, and the lattice will become more similar to a simple lattice than it is at low pressures. It is possible that this goes on continually, and that one reaches a simple close packed lattice with metallic properties only in the limiting case of infinite pressures.

During the increase of pressure, the total energy of the substance will increase by the work done (we assume very low temperatures). It is possible, thus, that the energy of the continuously compressed lattice becomes at a certain volume, assumed at a very high pressure, greater than that of another modification. In this case there will be a *discontinuous change* to the latter.[17] Whether or not such a transition will occur into the metallic modification, depends on the magnitude of the compressibility of the molecular form at high pressures. The smaller this is, the greater will be the pressure necessary for a certain change in volume, and also the energy increase at this compression. If the extremely high compressibility at ordinary pressures,[18] which is 2.10^{-9} cm²/dyne, would hold throughout, the molecular form would be stable for all volumes. This is not possible, however, and the compressibility certainly decreases with increasing pressure, but one cannot tell, at present, whether it decreases sufficiently to make the metallic form stable at *any* pressure. One calculates easily, that even under the assumption of the most advantageous compressibility at high pressures, the pressure necessary for the transformation is 250,000 atmos., which is outside the scope of the present technique.

The objection comes up naturally that we have calculated the energy of a body-centered metallic lattice only, and that another metallic lattice may be much more stable. We feel that this objection is justified. Of course it is not to be expected that another simple lattice, like the face-centered one, have a much lower energy,—the energy differences between these forms are always very small. It is possible, however, that a layer-like lattice has a much greater heat of formation, and is obtainable under high pressure. This is suggested by the fact that in most cases of Table I of allotropic modifications, one of the lattices is layer-like,[19] the other either metallic, valence, or molecular. The difficulties for such an experiment will be greatly increased by the necessity of the formation of a nucleus for the new lattice.

[15] The calculated nearest distance for the metallic form is 1.5A.

[16] F. London, Zeits. f. Elektrochemie **35**, 552 (1929); H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931).

[17] Such polymorphic transitions induced by pressure in solids are described by P. W. Bridgman, Rev. Mod. Phys. **7**, 1 (1935).

[18] Measured by A. Eucken for the liquid form, Ber. deutschen Phys. Ges. 4 (1916).

[19] Diamond is a valence lattice, but graphite is a layer lattice (A. W. Hull, Phys. Rev. **10**, 661 (1917)). Yellow arsenic and phosphorus are evidently molecular lattices, black phosphorus a layer lattice (R. Hultgren and B. E. Warren, Phys. Rev. **47**, 808 (1935)), and metallic As is also only approximately a simple lattice. The red, monoclinic selenium can be said to form a molecular lattice (F. Halla, F. Bosch, E. Mehl, Zeits. f. physik. Chemie **B11**, 455 (1930)), while the metallic modification is a thread lattice (A. J. Bradley, Phil. Mag. **48**, 477 (1924)). The situation seems to be most complicated with tin. Grey tin forms a diamond lattice, but shows otherwise no similarity to the valence lattice of diamond, while the metallic lattice has a rather complicated structure (H. Mark and M. Polanyi, Zeits. f. Physik **18**, 75 (1923)).

The Electron Affinity of Iodine from Space-Charge Effects[1]

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(Received September 25, 1935)

The electron affinity of iodine atoms has been determined by a direct method in which only iodine atoms and electrons were involved. The value so obtained is 74.6 k-calories, which is in good agreement with values obtained by other methods. *The concentration of the several ions of different masses (I^- and E^-) have been calculated from their effect on space charge.* It has been established that iodine has no effect on the thermionic emission of tungsten.

I. INTRODUCTION

MANY attempts have been made to determine directly the electron affinity of the elements and to this date comparatively few values have been obtained.[3] One of us[4] has described an empirical method of estimating the electron affinity of the light elements and it is our plan to check these empirical values by experiments in this laboratory. In the present paper we report an experimental determination of the electron affinity of iodine atoms obtained by a new method. We have determined the equilibrium of reaction

$$X+E^-\rightarrow X^-+\Delta E_0$$

at the surface of a hot tungsten filament and from the equilibrium constant we have succeeded in calculating the electron affinity: $-\Delta E_0$. As far as this fundamental principle is concerned it appears that Sutton and Mayer[5] have employed the same idea and for the same purpose. Since, however, the measurement of the important ratio of the ion to the electron current (I^- to E^-) in our work differs radically from the method used by these authors, we feel that we should present our results. Iodine was used in our study for the reason that its electron affinity is well known and hence any new experimental method can be tested by the use of this element.

[1] Presented at the New York Meeting of the A. C. S. April, 1935.

[2] This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Melvin Calvin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] O. Oldenberg, Phys. Rev. **43**, 534 (1933). This paper contains further references.

[4] Geo. Glockler, Phys. Rev. **45**, 111 (1934).

[5] Sutton and Mayer, J. Chem. Phys. **3**, 20 (1935).

II. THEORETICAL CONSIDERATIONS

The equilibrium constant

In the case of the ionization of caesium on tungsten Langmuir[6] was able to measure the equilibrium

$$Cs\rightarrow Cs^++E^--\Delta U_0 \qquad (1)$$

established at the surface of a hot filament, where ΔU_0 is the ionization energy derived from spectroscopic data. He obtained very good agreement with the theoretical value of the equilibrium constant calculated by the equation

$$K(Cs, n)=\frac{n(E^-)\times n(Cs^+)}{n(Cs)}=\frac{w(E^-)w(Cs^+)}{w(Cs)}\times\frac{(2\pi m(E^-)kT)^{\frac{3}{2}}}{h^3}\times e^{-\Delta U_0/RT}. \qquad (2)$$

The $n(x)$ are the concentration of the species "x" in numbers of particles per cc, the $w(x)$ are the statistical weights of the normal states, $m(x)$ are the weights in grams of the individual particles x and the other symbols have their usual meanings. If in our case the reaction occurring at the filament surface is

$$I^-\rightarrow I+E^--\Delta E_0 \qquad (3)$$

then

$$K(I^-, n)=n(I)\times n(E^-)/n(I^-). \qquad (4)$$

Since the electron affinity is defined for the reverse reaction, we shall write

$$k(I^-, n)=n(I^-)/n(I)\times n(E^-)=1/K(I^-, n) \qquad (5)$$

and from Eq. (2) we have

$$k(I^-, n)=[w(E^-)\times w(I)/w(I^-)\times(2\pi m(E^-)kT)^{\frac{3}{2}}/h^3\times e^{-\Delta E_0/RT}]^{-1}. \qquad (6)$$

[6] Langmuir, Phys. Rev. **43**, 226 (1933).

If, then, $k(I^-, n)$ can be determined experimentally, the electron affinity of iodine can be obtained from Eq. (6). The constant $k(I^-, n)$ can be obtained from Eq. (5) if the concentrations of the interacting species can be determined. $n(I)$ can be obtained from the vapor pressure of iodine assuming that every molecule striking the filament surface is dissociated into two atoms[5] and the ratio $n(I^-)/n(E^-)$ can be obtained from the space-charge equation. *It is in the determination of this ratio that our method differs from the work of Sutton and Mayer.*[5] While they employed a magnetron set-up to differentiate between the ion and electron current, we employed the current-potential relations of a space-charge region to evaluate them.

The space-charge equation

The space-charge limited current between a pair of electrodes is given by the well-known Langmuir-Child equation[7]

$$\log i = \log C(e/m)^{\frac{1}{2}} + \tfrac{3}{2} \log V, \tag{7}$$

where C is a geometrical constant, e/m is the ratio of charge to mass of the carriers of the current and V is the potential difference between the electrodes. By taking current-voltage data in vacuum where electrons only carry the current and plotting $\log i$ against $\frac{3}{2} \log V$ we can determine the geometrical constant C for any experimental conditions. By plotting similar data obtained with iodine present between the electrodes an effective value of e/m can be calculated which will be different from that of the electrons and will depend on the number of other types of charged ions present between the electrodes.

In order to determine the relationship between the effective e/m of Eq. (7) and the number of heavy negative ions (I^-) present we must reconsider the derivation of this equation. It is obtained from Poisson's equation

$$\nabla^2 V = 4\pi\rho, \tag{8}$$

and for cylindrical electrodes:

$$2\pi r\rho = i/u = i(m/2eV)^{\frac{1}{2}}, \tag{9}$$

where ρ is the negative charge density and u is the velocity of the charged particle: $((2eV)/m)^{\frac{1}{2}}$. Eqs. (8) and (9) yield[8]

$$r d^2V/dr^2 + dV/dr = (2m/eV)^{\frac{1}{2}} i, \tag{10}$$

which gives on integration from $r=0$ to $r=r$, $(dV/dr)=0$ and $V=0$ at $r=0$:

$$i = 2\sqrt{2}/9r(e/m)^{\frac{1}{2}} V^{\frac{3}{2}}$$

or

$$\text{const} \times V^{\frac{3}{2}} = i(m/e)^{\frac{1}{2}}. \tag{11}$$

In the special case we are considering we shall assume that there are present ions of two masses: $m(E^-)$ and $m(I^-)$. There will be then two currents: $i(E^-)$ and $i(I^-)$ and

$$\rho = \rho(E^-) + \rho(I^-) = i(E^-)/u(E^-) + i(I^-)/u(I^-),$$

or

$$\rho = (1/\sqrt{2})\{i(E^-)(m(E^-)/e)^{\frac{1}{2}} + i(I^-)(m(I^-)/e)^{\frac{1}{2}}\} V^{-\frac{1}{2}}. \tag{12}$$

The form of this expression is the same as Eq. (9) with $i(E^-)(m(E^-)/e)^{\frac{1}{2}}$ replaced by $\{i(E^-)(m(E^-)/e)^{\frac{1}{2}} + i(I^-)(m(I^-)/e)^{\frac{1}{2}}\}$. Since these terms have the same functional relation to V and are subject to the same boundary conditions, the integration will be exactly analogous and we can write the solution directly

$$\text{const} \times V^{\frac{3}{2}} = i(E^-)(m(E^-)/e)^{\frac{1}{2}} + i(I^-)(m(I^-)/e)^{\frac{1}{2}}. \tag{13}$$

Hence the effective value of m/e as determined from experiment is related to its constituents as follows:

$$i(m/e)^{\frac{1}{2}} = i(I^-)(m(E^-)/e)^{\frac{1}{2}} + i(I^-)(m(I^-)/e)^{\frac{1}{2}}, \tag{14}$$

and

$$i = i(E^-) + i(I^-) \tag{15}$$

and

$$\frac{i(I^-)}{i(E^-)} = \frac{m^{\frac{1}{2}} - (m(E^-))^{\frac{1}{2}}}{(m(I^-))^{\frac{1}{2}} - m^{\frac{1}{2}}} = F = \frac{\mu(I^-) \times e}{\mu(E^-) \times e}, \tag{16}$$

where $\mu(I^-)$ is the number of I^- crossing unit area in unit time between filament and plate and $\mu(E^-)$ is the corresponding quanity for electrons.

The equilbrium equation

It is well known from kinetic theory that the concentration of a species is related to the number traversing unit area in unit time, by

[7] O. W. Richardson, *Emission of Electricity from Hot Bodies* (Longmans, Green & Co., London, 1921).

[8] Langmuir and Compton, Rev. Mod. Phys. **3**, 191 (1931); and Langmuir, Phys. Rev. **2**, 450 (1913).

$$\mu(x)=n(x)(kT/2\pi m(x))^{\frac{1}{2}}. \qquad (17)$$

The mass of I^- is sensibly the mass of I atom and since the three particles (I, I^-, E^-) are formed at the filament their temperature is the temperature of the filament: T_s. The number of iodine atoms formed at the filament is twice the number of I_2 molecules striking it:

$$\mu(I_2)=P(I_2)/(4\pi m(I)kT_G)^{\frac{1}{2}}, \qquad (18)$$

where $P(I_2)$ is the pressure of iodine molecules in baryes and T_G is the temperature of the iodine gas (about room temperature). The equilibrium constant (Eq. (5)) can now be written:

$$k(I^-,n)=\frac{Fk}{P(I_2)}\times\left[\frac{m(I)T_G}{2m(E^-)}\right]^{\frac{1}{2}}\times T_s^{\frac{1}{2}}\times\frac{3\times10^{-10}}{4}, \qquad (19)$$

and combined with Eq. (6) permits the calculation of the electron affinity.

III. Experimental Procedure

The experimental set-up is shown in Figs. 1 and 2 and consists of a diode (filament and plate) with an iodine reservoir. The filament is a tungsten wire 0.1 mm thick and about 42 mm long. The plate is made of tantalum (0.152 mm thick) and is in the form of a cylinder 45 mm high and 21.4 mm diameter. The glass tube is 35.6 mm in diameter. The details of the electrical connections are shown in Fig. 1. The experimental set-up is essentially that used by Heinze[9] in measuring the work function by the cooling method. It is a Wheatstone bridge with audiofrequency current for balancing and direct current for heating the filament which forms one of the arms of the bridge. The various parts of the electrical arrangement are:

Am, ammeter measuring approximately the current through the bridge.

A,B, endcoils of Leeds and Northrup Kohlrausch bridge each having a resistance of 124.14 ohms.

C_1, blocking condenser having a capacitance of about one mf.

C_2, variable condenser having a range of 0.00003–0.04 mf. It is necessary to balance out any capacitance that might be introduced into the bridge by the experimental tube or at other points.

E_1, experimental tube.

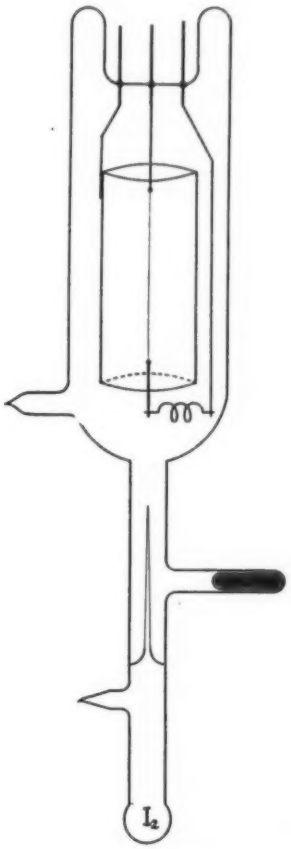

Fig. 1. Reaction tube.

F_1, parallel resonance circuit tuned to the frequency of the oscillator and thus providing an infinite impedance to the audiofrequency attempting to get through the plate circuit and preventing this auxiliary current from falsifying the bridge measurements.

F_2, the filament of the experimental tube.

I, manganin slide wire in mercury (10 ohms).

K, slide wire of Leeds and Northrup Kohlrausch bridge (type 54161). Its resistance was checked on a standard bridge of the Physics Department and is 27.72 ohms.

L_1, lead storage "B" batteries.

L_2, set of four two hundred-ampere hour lead storage cells. They could be arranged in any series or parallel combination so as to deliver up to 24 volts. It is very essential that these batteries be capable of maintaining a current of about 1.5 amperes steady to within 0.005 ampere over a period of one hour.

M, manganin slide wire in mercury (one ohm).

M.A., microammeter with shunts capable of measuring currents from $2\times10^{-7}-3\times10^{-2}$ amp. It measures the plate current.

[9] Heinze, Ann. d Physik **16**, 41 (1933).

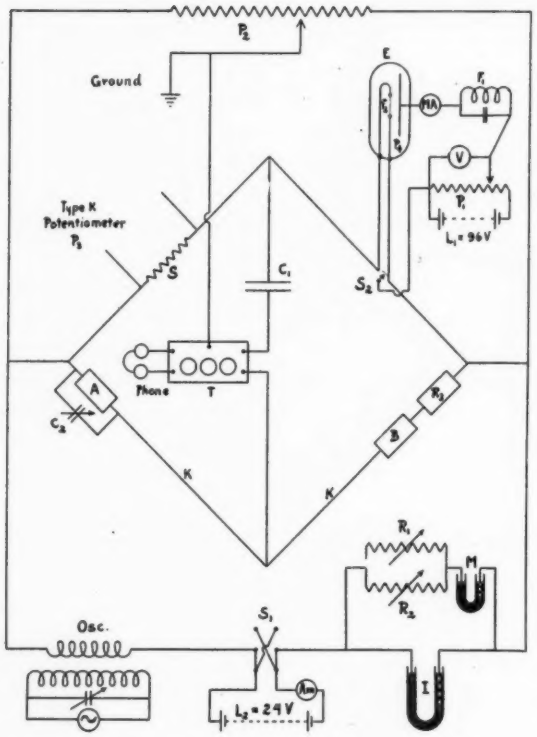

FIG. 2. Electrical connections.

Osc, vacuum tube oscillator which supplies the audio-frequency current to activate the bridge.
P_1, potentiometer (2700 ohms).
P_2, potentiometer (10,000 ohms) used as a Wagner ground on the bridge.
P_3, type "K" Leeds and Northrup potentiometer across the standard resistance "*S*." It is used to make the critical measurement of the current through the filament.
P_4, the plate of the experimental tube.
R_1, variable resistance (100 ohms) for controlling the current through the filament.
R_2, variable resistance (25 ohms).
R_3, standardized three-dial noninductive resistance (999 ohms). It is necessary in order to achieve a balance when the end coils are in.
S, one-ohm Leeds and Northrup standard resistance.
S_1, reversing switch for reversing the current through the bridge.
S_2, arrangement for connecting the negative terminal of the "B" battery to either end of the filament.
T, three-tube amplifier with telephone used as the balance detector of the bridge.
V, voltmeter for plate voltage.

The tube was outgassed by standard procedure and the work function of tungsten was determined by two methods.

The work function of tungsten

The work function of the filament material (tungsten) was obtained from the temperature variation of the saturation current by the use of well-known relations. The object was to ascertain that the filament surface was clean. The value for the work function was found to be 4.59 electron volts which is in very close agreement with the accepted value for pure tungsten. The second method employed was a measurement of the cooling effect on the filament due to the evaporation of the electrons. The value obtained is 4.60 electron volts in excellent agreement with the value obtained from the Richardson equation. The temperature of the filament was obtained from the heating current and the Langmuir table.[10]

These measurements established the following facts: (1) The apparatus will actually measure heat values at the surface of the filament. (2) The methods used in the measurements of the various experimental quantities and the estimated corrections (for example end losses etc.) are valid. (3) The material of the filament is satisfactory, i.e., clean. (4) The tube is free from residual gases.

Admission of iodine

The tube having been prepared by outgassing and filament-aging was then filled with iodine vapor. After the iodine was admitted the filament was again allowed to age for at least thirty hours, always keeping liquid air on the tube containing the solid iodine supply. At this point the filament was subjected to the emission test and it was found to be unaltered. Moreover raising the iodine pressure even as high as 10^{-4} mm Hg had no effect on the saturation emission characteristics of the filament. This seems entirely reasonable for before a molecule can affect the thermionic emission from a surface it must be adsorbed on the surface. At our high filament temperatures (above 2000°K) iodine atoms are not adsorbed. This finding is in agreement with the work of Van Pragh[11] who studied the accommodation coefficient of helium on platinum which had been subjected to various treatments in iodine. He found that platinum treated in

[10] Langmuir and Jones, Gen. Elec. Rev. **30**, 310–9 (1927).
[11] Van Pragh, J. Chem. Soc. 798 (1933).

iodine above 1650°K showed an accommodation coefficient toward helium corresponding to that of a clean surface. But when iodine was allowed to come into contact with the platinum at any lower temperature, the accommodation coefficient changed immediately to that of a platinum surface covered with a layer of iodine. Since tungsten iodide is much less stable than platinum iodide it seems reasonable to say that at our high temperatures *iodine has no effect on the thermionic emission from tungsten*. This is in agreement with statements made by Langmuir in private communications to others.[12]

But it still remains true that the presence of the iodine vapor between the electrodes can and does influence the plate current. In the space-charge limited region and below the ionization potential of iodine (molecule or atom) the current is affected by the creation of heavy negative ions (I^- etc.) which help to increase the negative space-charge density and thus decrease the electron current. As soon as the ionization potential is reached positive ions are formed, the negative space charge is neutralized and the plate current jumps above its value in a vacuum. If the number of positive ions is large enough the saturation current may even be larger than that in a vacuum.

Current-voltage relation in iodine

The data needed for the calculation of the electron affinity are simply a set of current-voltage tables taken in the space-charge limited region and at voltages less than the ionization potential of iodine. This information together with the temperature of the filament, the pressure of the iodine at which the measurement was taken and the gas temperature is all that is needed for the calculation of the electron affinity.

The filament temperature is first set with liquid air on the iodine supply. The Wheatstone bridge in which the filament is located is balanced and the plate current is measured as a function of plate voltage. The iodine is then admitted to any desired pressure by warming the side tube in the proper bath. The filament will cool off because of the thermal conduction of the iodine vapor.

[12] Van Pragh and Rideal, Proc. Roy. Soc. **A134**, 385 (1931), and reference 5.

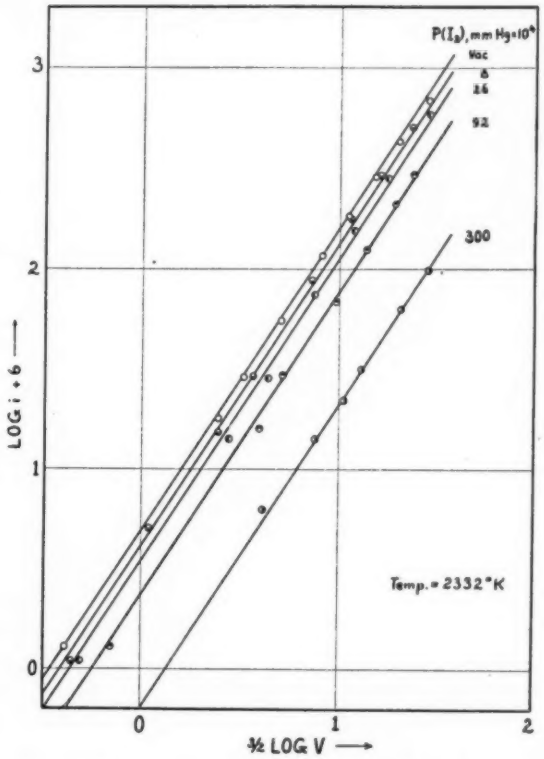

FIG. 3. Current-voltage relations in iodine.

This cooling effect causes a drop in resistance of the filament which will become apparent on the Wheatstone bridge. *By increasing the filament heating current so as to reestablish the filament resistance originally found in a vacuum, we assume that the filament temperature is returned to its original value.* Again we find the plate-current as a function of plate voltage under the new conditions and repeat the procedure for several pressures of iodine. For each filament temperature a new set of vacuum data must be taken. A sample run is shown in Table I. The filament temperature is 2332°K. The data are plotted in Fig. 3.

IV. Discussion of Results

The current ratio *F*

The data given in Table I and shown in Fig. 3 are used to calculate effective values of m which satisfy the Langmuir-Child equation under any given set of conditions and hence the value of F the ratio of the current carried by the iodide ions

TABLE I. *Current-voltage relation in I_2, filament temperature 2332°K.*

Iodine temp. & pressure (°C & mm Hg)	Plate current (amp. $\times 10^6$) i	Plate voltage (volts) V	Iodine temp. & pressure (°C & mm Hg)	Plate current (amp. $\times 10^6$) i	Plate voltage (volts) V
−180°C	1.3	0.55	−31.0°C	1.1	0.58
($<10^{-6}$)	5.1	1.06	0.0008	15.4	1.82
	17.9	1.82		29.4	2.38
	28.9	2.22		89.0	3.76
	55.0	2.95		176.0	5.08
	117.0	4.06		293.0	6.38
	184.0	5.01		510.0	8.17
	288.0	6.15	−21.1°C	1.1	0.62
	430.0	7.38	0.0026	14.2	1.98
	690.0	9.34		29.1	2.67
−40°C	1.9	0.72		75.0	3.84
0.00018	15.7	1.73		156.0	5.23
	27.4	2.22		283.0	6.78
	87.0	3.63		590.0	9.34
	179.0	5.00	−10.45°C	1.3	0.79
	282.0	6.13	0.0092	16.0	2.51
	610.0	8.82		29.5	3.23
				69.0	4.55
				125.0	5.75
				211.0	7.16
				295.0	8.25

(I^-) and the electrons (E^-). From Eq. (7) we see that the intercept on the log i-axis of Fig. 3 gives the constant $C(e/m)^{\frac{1}{2}}$. The straight line referring to the conditions in a vacuum shows of course the relation when electrons only are carrying the current. Hence e/m is that of the electron $(4.774\times10^{-10}\times6.06\times10^{23}\times1845\times1.008^{-1}=7.27\times10^{8})$. For the case shown in Fig. 3 we find for a vacuum

$$\log C(e/m)^{\frac{1}{2}}=0.66-6.00=4.66-10,$$

and $$C(e/m)^{\frac{1}{2}}=4.57\times10^{-6}$$

hence $$C=4.57\times10^{-6}/7.27\times10^{8}=6.28\times10^{-15}$$

in units where electric charge is in electrostatic units and masses in weights of atoms in grams. With iodine in the tube at a pressure of 9.2×10^{-3} mm Hg we find the straight line log i *vs.* volts to intersect the log i axis at a point

$$\log C(e/m)^{\frac{1}{2}}=0.33-6=4.33-10$$

or $$C(e/m)^{\frac{1}{2}}=2.14\times10^{-6}.$$

Using the value of C found above we obtain

$$(e/m)^{\frac{1}{2}}=2.14\times10^{-6}/6.28\times10^{-15}=3.41\times10^{8}.$$

Considering the carriers singly charged we use

$$e^{\frac{1}{2}}=(4.774\times10^{-10})^{\frac{1}{2}}=2.19\times10^{-5}$$

and $$e^{\frac{1}{2}}/(e/m)^{\frac{1}{2}}=m^{\frac{1}{2}}=\frac{2.19\times10^{-5}}{3.41\times10^{8}}=6.43\times10^{-14}.$$

We need to know

$$(m(E^-))^{\frac{1}{2}}=[1.008/(1845\times6.06\times10^{23})]^{\frac{1}{2}}$$
$$=3\times10^{-14}$$

and $$(m(I^-))^{\frac{1}{2}}=[127/(6.06\times10^{23})]^{\frac{1}{2}}$$
$$=1.45\times10^{-11}$$

in order to evaluate F from Eq. (16):

$$F=\frac{6.43\times10^{-14}-3.0\times10^{-14}}{1.45\times10^{-11}-6.43\times10^{-14}}=2.37\times10^{-3}.$$

This procedure is repeated for each iodine pressure, a new geometrical constant being determined at each filament temperature.

Calculation of electron affinity

Eqs. (6) and (19) can be used to calculate the electron affinity. The following values of constants appearing in the equation were used: The statistical weight of the electron $w(E^-)$ is 2; the normal state of the iodine atom is $^2P_{3/2}$ and hence $w(I)=4$ and for the iodine ion the ground state is S_0 giving $w(I^-)=1$; $k=1.371\times10^{-16}$; $m(E^-)=9\times10^{-28}$; $h=6.55\times10^{-27}$; $m(I)=20.94\times10^{-23}$; $T_G=300°K$; $e=2.71828$. The final equation becomes

$$-\Delta E_0=4.575\,(\log F+2\log T_s - \log P(I_2)+1.075). \quad (20)$$

The results of our experiments are summarized in Table II. The measurements extend over a

TABLE II. *Electron affinity of iodine.*

Experiment No.	Filament temperature T_s (°K)	Iodine pressure $P(I_2)$ (mm Hg $\times10^6$)	Current ratio F ($\times10^4$)	Electron affinity $-\Delta E_0$ (k-calories)
1	2400	8.50	2.12	79.2
2	"	2.80	3.45	75.7
3	2395	3.78	4.00	75.1
4	"	30.00	27.50	74.2
5	2332	0.18	1.03	80.5
6	"	0.80	3.65	79.3
7	"	2.60	8.22	77.8
8	"	9.20	23.70	76.7
9	"	30.00	71.80	75.4
10	2031	3.15	12.21	67.7
11	"	30.00	87.70	66.6
12	2020	0.85	106.2	72.0
13	"	2.70	163.5	69.2
				average: 74.6 kcal.

temperature range of 380°K and involve a 166-fold change in iodine pressure.

Concluding remarks

In the development of the relation between the effective mass of the carriers of electricity (m) and the ratio (F) of ion to electron current we assumed that there were present only two kinds of ions: I^- and E^-. The possibility of the formation of heavier negative ions I_2^- and I_3^- immediately arises. Should these ions exist in the tube in quantity, then the F values would be two large and hence result in high values of $-\Delta E_0$. Since the average value obtained for the electron affinity is apparently not too high, we conclude that our original assumption is correct. This is further supported by the work of Hogness and Harkness[13] who have shown that in the low voltage arc in iodine, the only result of a primary process is I^- and that I^- is the result of the only primary process. They have shown that I_2^- and I_3^- exist only in very small quantity and that they arise by secondary processes after I^- has been formed.

Another assumption that was made in obtaining the equilibrium equation, is that every iodine molecule that strikes the surface of the filament is dissociated. This is also justified by the results obtained. Langmuir in a private communication to others[5] has stated that such is the case. It should also be noted that the heat of dissociation of iodine is only 1.5 electron volts. The work of Stark and Bodenstein[14] indicates that iodine vapor at low pressure would be almost completely dissociated at 1200°C. The filaments used were all above 2000°K and since it is reasonable to assume that the filaments used are not perfectly smooth so that each molecule has a very good chance to approach temperature equilibrium with the filament, it is to be expected that almost every molecule striking the surface will be dissociated. There is only one piece of evidence to the contrary. Van Pragh and Rideal[15] in their experiments on the attack of platinum and tungsten by the halogen vapors come to the conclusion that the dissociation even at our high temperatures is given by

$$\mu(\mathrm{I}) = 2\mu(\mathrm{I}_2) \times e^{-D/RT}, \qquad (21)$$

where D = dissociation energy of iodine molecules. No explanation for this discrepancy has been suggested. In our work it may be assumed that the results indicate complete dissociation of every iodine molecule striking the hot filament.

The possibility exists that the electrons suffer reflection at the filament surface. This situation has already been discussed by Sutton and Mayer.[5] Our experiments are not accurate enough to shed light on this point. From the results obtained it may be seen that the various assumptions made must be reasonably correct, since the value of electron affinity found checks the results of other methods satisfactorily.

[13] Hogness and Harkness, Phys. Rev. **32**, 784 (1928).

[14] Stark and Bodenstein, Zeits. f. Elecktrochemie **16**, 961 (1910).

[15] Van Pragh and Rideal, Proc. Roy. Soc. **A134**, 385 (1931).

Nonadiabatic Reactions. The Decomposition of N_2O

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(Received September 30, 1935)

The experimental and theoretical absolute rates for the nonadiabatic decomposition of N_2O are shown to be in good agreement. The amount of chemical inertia present in other reactions involving the singlet-triplet transition of oxygen is considered. A convenient method of constructing potential functions for polyatomic molecules which fit the spectroscopic data, and which reduce in the proper way for the various dissociation processes, is indicated, and is carried through for the N_2O molecule.

THE method of calculating absolute reaction rates by means of statistical mechanics as developed at the present time[1] involves information obtainable from potential surfaces. For a large number of reactions interest is confined to the lowest surface. There are also cases of importance for which, when magnetic effects are neglected, two potential surfaces intersect. When these effects are considered the surfaces, instead of crossing, approach each other very closely. In such cases the reacting system may pass from one of the noncrossing surfaces to the other in the neighborhood of the point of closest approach instead of proceeding across the potential barrier, and thus may fail to react. The fraction of the systems reaching the activated state which react we take equal to κ. The transmission coefficient, κ, plays exactly the role of c in Eq. (10) of reference 1.

Nonadiabatic reactions have been considered by a number of authors.[2] As an example of such a reaction the dissociation of nitrous oxide into a nitrogen molecule and an oxygen atom will be considered. That the N_2O reaction proceeds abnormally slowly for a unimolecular reaction is well known from the work of Volmer and his collaborators.[3] Wigner and others[4] have remarked that the reaction might be expected to proceed only about 0.001 as fast as the normally expected rate because of the change of multiplicity in the decomposition. In the ordinary thermal process a nonparamagnetic linear NNO molecule passes from a $^1\Sigma$ state through an activated state 53 kg. cal. higher to form $O(^3P)$ and $N_2(^1\Sigma)$.

We next consider the properties of the molecular potential energy. Among the conditions which we require for a satisfactory potential function for N_2O in its normal state are:

(1) Removal of an O atom to infinity must leave the function for a normal N_2 molecule.

(2) Removal of an N atom to infinity must reduce the potential to that for a $^4\Sigma$ NO molecule.

(3) N_2O being a linear molecule with O on one end, the function must yield the same values for an O atom approaching either N atom.

(4) The minimum must correspond to the correct dissociation energy and moment of inertia (interatomic distances).

(5) The potential must yield the known vibration frequencies.

Certain less obvious conditions on the potential are next considered. When N_2O decomposes adiabatically to give a $^1\Sigma$ N_2 molecule the oxygen will of necessity be in a singlet state. Now O (^1D) lies 45.1 kg. cal. above O (^3P),[5] whereas the next higher level, O (^1S) lies 96.1 kg. cal. above the ^3P state. Because O (^1S) is so much higher than O (^1D) we conclude that the state of oxygen in the normal N_2O is such that if it dissociated without change of multiplicity into $^1\Sigma$ N_2 and therefore singlet oxygen the latter would be in a ^1D state. Now N_2 ($^1\Sigma$) dissociates adiabatically into two nitrogen atoms each in a ^4S state. Thus one thinks of a $^1\Sigma$ N_2O as assembled without change of multiplicity from two

[1] Eyring, J. Chem. Phys. **3**, 107 (1935).

[2] a. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932). b. Zener, Proc. Roy. Soc. **A137**, 696 (1932); **A140**, 660 (1933). c. Landau, Physik. Zeits. Sowjetunion **1**, 88 (1932); **2**, 46 (1932). d. London, Zeits. f. Physik **74**, 143 (1932). e. Hellmann and Syrkin, Acta Physicochimica **2**, 433 (1935).

[3] a. Volmer and Kummerow, Zeits. f. physik. Chemie **B9**, 141 (1930). b. Nagasako and Volmer, ibid. **B10**, 414 (1930). c. See also Hunter, Proc. Roy. Soc. **A144**, 386 (1934).

[4] a. Wigner, Nachr. Ges. Wiss. Göttingen, p. 375 (1927). b. Pelzer and Wigner, Zeits. f. physik. Chemie **B15**, 445 (1931–32). c. Eyring, Chem, Rev. **10**, 103 (1932). d. G. Herzberg, Zeits. f. physik. Chemie **B17**, 68 (1932).

[5] Bacher and Goudsmit, *Atomic Energy States* (New York, McGraw-Hill, 1932).

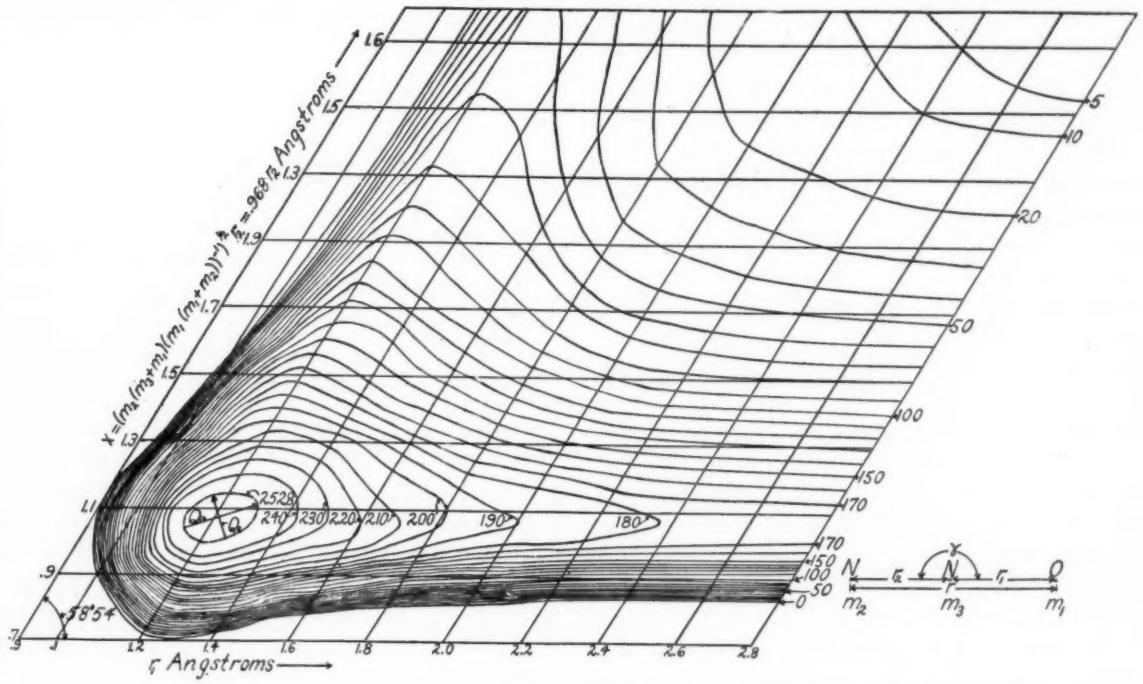

FIG. 1. Potential energy surface for N_2O for linear configurations. Contours, 10 kg. cal. intervals.

^4S nitrogen atoms and one ^1D oxygen atom. When a ^4S nitrogen is removed from N_2O adiabatically it must leave a $^4\Sigma$ NO molecule behind which is formed from a ^4S nitrogen atom and a ^1D oxygen atom. This corresponds to the NO $(\sigma\pi^4\pi^2, {}^4\Sigma^-)$ of Mulliken.[6] We use as his estimated values for the constants for the corresponding Morse curve an equilibrium distance $r_0=1.28$A, a vibration frequency $\omega=3000r_0^{-3}=1430$ cm^{-1} and a heat of dissociation plus zero-point energy of 40 kg. cal. The zero-point energy of 2 kg. cal. leaves 38 kg. cal. for the heat of dissociation.

We shall use a potential function $V(r_1, r_2, \gamma)$ for N_2O in which the coordinates and masses are as indicated in Fig. 1.

The following definitions are introduced for convenience, where it is to be understood that the partial derivatives are to be evaluated at the point $r_1=1.22$; $r_2=1.10$; and $\gamma=180°$.

$$k_1=\left(\frac{\partial^2 V}{\partial r_1^2}\right),\quad k_2=\left(\frac{\partial^2 V}{\partial r_2^2}\right),\quad k_{12}=\left(\frac{\partial_6 V}{\partial r_1\partial r_2}\right),\quad k_3=\left(\frac{\partial^2 V}{\partial \gamma^2}\right),$$

$$\mu_1=(m_1m_2+m_1m_3)(m_1+m_2+m_3)^{-1},$$

$$\mu_2=(m_1m_2+m_2m_3)(m_1+m_2+m_3)^{-1},$$

$$\mu_3=m_1m_2(m_1+m_2+m_3)^{-1},$$

$$b_{33}=r_1^2r_2^2(\mu_1\mu_2-\mu_3^2)(\mu_1r_1^2+\mu_2r_2^2+2\mu_3r_1r_2)^{-1}$$

and

$$\lambda_i=2\pi c\omega_i,$$

where c is the velocity of light and ω_i is the ith frequency of N_2O in wave numbers.

Now a straightforward solution of the mechanical problem for three atoms (see Cross and Van Vleck)[7] relates the frequencies to the force constants by the following equation.

$$\begin{vmatrix} \mu_1\lambda^2-k_1 & \mu_3\lambda^2-k_{12} & 0 \\ \mu_3\lambda^2-k_{12} & \mu_2\lambda^2-k_2 & 0 \\ 0 & 0 & b_{33}\lambda^2-k_3 \end{vmatrix}=0. \qquad (1)$$

The fact that N_2O is linear is responsible for Eq. (1) reducing to a linear and a quadratic equation. The k's are now determined to fit the observed frequency as given by Plyler and Barker.[8] For the two equal (degenerate) bending frequencies these authors give 589 cm^{-1}, so that $k_3=6.4\times10^{-12}$ ergs mol.$^{-1}$ rad.$^{-2}$. They give

[6] Mulliken, Rev. Mod. Phys. **4**, 51 (1932). (See Fig. 48.)

[7] Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).

[8] Plyler and Barker, Phys. Rev. **38**, 1827 (1931).

$\omega_1=1285.4$ and $\omega_2=2224.1$ cm^{-1} for the other two frequencies. These two values, then, fix the two roots, λ^2, of the quadratic. Since there are three k's to determine however, and since in any case k_{12} must be comparatively small, we try taking it equal to zero. This leads to complex values for k_1 and k_2 which are impossible. Thus we cannot neglect the interaction between the two outer atoms. We eliminate one k by the requirement that $k_1/k_2=15.85\times10^5(22.2\times10^5)^{-1}$, which is the ratio of the force constants of a normal NO and a normal N_2 molecule.[9] This gives $k_1=12.0\times10^5$, $k_2=16.7\times10^5$ and $k_{12}=0.9\times10^5$. The units are in ergs mol.$^{-1}$ cm^{-2}.

For the equilibrium distances in the N_2O molecule we take the values proposed by Pauling,[10] i.e., for the N–N distance $r_2=1.10$A, and for the N–O distance $r_1=1.22$A. These values give a moment of inertia of 66.7×10^{-40} as compared with 66.0×10^{-40} found by Barker.[11]

We now give a potential function for N_2O which satisfies all the conditions enumerated except the third. It is

$$V=D_1f(a_1, r_1, b_1)+D_2f(c_2, r_2, d_2)$$
$$+\sum_{i=3}^{7}D_if(a_i, r_1, b_i)f(c_i, r_2, d_i)$$
$$+D_8f(a_8, r_1, b_8)f(c_8, r_2, d_8)\sin^2\gamma. \quad (2)$$

Here

$$f(a, r_1, b)=\exp-(2a(r_1-b))-2\exp-(a(r_1-b))$$

and

$$f(c, r_2, d)=\exp-(2c(r_2-d))-2\exp-(c(r_2-d)).$$

If to (2) we add all the additional terms obtained by replacing r_1 by r_3 and γ by δ, where δ measures the angle between r_2 and r_3, then the third condition is also satisfied. The inclusion of these terms considerably complicates our potential without changing it appreciably in the region in which we are interested so that they are omitted.

The constants used in Eq. (2) are collected in Table I.

TABLE I. *Constants used in potential function (2).*

	D	a	b	c	d
1	40.	3.95	1.28	—	—
2	172.82	—	—	3.10	1.09
3	−39.97	3.00	1.12	3.00	1.20
4	−57.89	3.00	1.12	3.00	1.10
5	25.97	3.95	1.22	3.00	1.20
6	74.27	3.00	1.22	4.00	1.10
7	−60.00	2.519	1.22	1.665	1.10
8	46.83	3.00	1.22	3.00	1.10

The adjustment of the constants for a function of the type (2) is a simple matter but should be made in a certain sequence.

(1) The first two terms are simply Morse functions for Mulliken's NO ($\sigma\pi^4\pi^2$, $^4\Sigma^-$) and for the normal nitrogen molecule, respectively.

(2) The third term takes care of k_{12}. The constants a_3 and c_3 are chosen as 3, approximately the value of a_2 in nitrogen. b_3 was chosen to contract the N−O bond while d_3 has the effect of slightly expanding the N−N bond. After these choices were made, D_3 is taken to make $k_{12}=0.9\times10^5$ ergs mol.$^{-1}$ cm^{-2}.

(3) The fourth term is chosen to make $\partial V/\partial r_1=0$ at $r_1=1.22$A and $r_2=1.10$A. Now d_4 is taken equal to 1.10 so that $f(c_4, r_2, d_4)=-1$. Finally a_4 and b_4 are kept with the values of a_3 and b_3 for the same reason as before and D_4 is so chosen as to make $\partial V/\partial r_1=0$.

(4) The fifth term is arranged in a manner analogous to the fourth to make $\partial V/\partial r_2=0$ for $r_1=1.22$A and $r_2=1.10$A.

(5) In the sixth and seventh terms k_1, k_2 and E are fitted. Here b_6 and b_7 are set equal to 1.22, the equilibrium N–O distance in N_2O, and d_6 and d_7 equal to 1.10 the corresponding N–N distance. Thus, for $r_1=1.22$ and $r_2=1.10$, for these two terms,

$$f(a, r_1, b)=f(c, r_2, d)=-1$$
$$\partial f(a, r_1, b)/\partial r_1=\partial f(c, r_2, d)/\partial r_2=0$$

and

$$\partial^2 f(a, r_1, b)/\partial r_1^2=2a^2D,$$

while

$$\partial^2 f(c, r_2, d)/\partial_2^2=2c^2D.$$

In this way the contribution to the energy is D_6+D_7. These are then chosen to give N_2O the correct dissociation energy and at the same time to give values for the a's and c's in the neighbor-

[9] Mulliken, Rev. Mod. Phys. **4**, 1 (1932).
[10] Pauling, Proc. Nat. Acad. Sci. **18**, 293, 498 (1932).
[11] Barker, Phys. Rev. **41**, 369 (1932).

hood of 3. a_6 and a_7 are now chosen so that $\partial^2V/\partial r_1^2=k_1$: and c_6 and c_7 so that $\partial^2V/\partial r_2^2=k_2$.

(6) The final term, of course, adds nothing to energy, slope or curvature in the r_1 and r_2 directions so long as the molecule is linear, i.e., $\gamma=0$ or π. D_8 is obtained by solving the equation $b_{33}\lambda^2=k_3$, and putting $D_8=\frac{1}{2}k_3$. There is some arbitrariness particularly in our choice of a_8 and c_8. This could be removed by fitting the potential function to give more exactly the higher frequencies found by Plyler and Barker in the manner employed by Adel and Dennison for CO_2.[12] A simple central force potential of the type they have used for CO_2 will not, in general, be valid for distances far from the equilibrium position, as they also point out. Our potential can hardly be seriously in error providing adiabatic decomposition gives the products we have supposed.

The method of using polynomials in the f's for the various bonds provides a way for constructing potential functions to fit all the limiting conditions for even the most complicated polyatomic molecules. This should be a generally useful procedure.

Fig. 1 gives the potential surface for linear N_2O plotted from Eq. (2). Here r_1 is plotted against r_2/f where $f=[m_1(m_3+m_2)/m_2(m_1+m_3)]^{\frac{1}{2}}$, and the angle between the abscissae and ordinates is given by

$$\pi/2-\sin^{-1}[m_2m_1/(m_3+m_2)(m_1+m_3)]^{\frac{1}{2}}=58°\ 54'.^{13}$$

The potential function (2) gives for the two nonbending normal coordinates

$$Q_1=0.4679(r_1-r_{01})+0.8828(r_2-r_{02})$$

and

$$Q_2=0.7842(r_1-r_{01})-0.6206(r_2-r_{02}).$$

Here r_{01} and r_{02} are the equilibrium distances. These give the directions of the major and minor axes of an equipotential line in the immediate neighborhood of the minimum if one plots it in the way used in Fig. 1. Because the potential involves terms higher than the second power in r_1 and r_2, by the time one has reached an equipotential corresponding to the zero-point energy (6.66 kg. cal.) the major and minor axes of the near ellipse will have changed. However, even in the present unsymmetrical case, this change in the coefficients of the r's is less than one percent. In the same way we expect our vibration frequencies to show a parallel small anharmonicity.

We next consider how the potential surface for O (^3P) approaching N_2 ($^1\Sigma$) will cut the surface just drawn. At large distances the O attracts the near N in N_2 due to the van der Waals forces and the Coulombic integrals, but it repels it by an amount equal to $\frac{1}{2}$ all the exchange integrals between the two atoms.[14] Now we take the attractive potential as 0.14 of the Morse curve value for NO in its normal state ($\sigma^2\pi^4\pi$, $^2\Pi$ in Mulliken's notation) and the repulsive potential as 0.43 of this value, giving a net repulsion of 0.29 of the Morse curve value.[14a] For this Morse curve we take $\omega=1906$ cm^{-1}, $r_0=1.15$A, $a=3.05$, heat of dissociation $=121.94$ kg. cal. and the zero-point energy $=2.71$ kg. cal. In Fig. 2 the curve I is a section following the lowest part of the east west valley of Fig. 1, while curve II is -0.29 times the Morse curve values for normal NO.

Absolute Rate of Reaction

Curves I and II intersect when r_1, the N–O distance, is 1.73A. This point of intersection of I and II is the activated state for the decomposition of N_2O. In the activated state the vibration in the r_1 direction becomes a translation, and our potential function gives us for the N to N vibration the value 2005 cm^{-1}, while the degenerate bending vibration has become 361 cm^{-1}. This gives us 3.9 kg. cal. for the zero-point energy in the activated state and an activation energy at the absolute zero of 50.0 kg. cal.

Now not every system passing through the activated state will make the transition from I to II. If we indicate the chance of transition, averaged over the velocity distribution characteristic of the temperature, by κ, we have for the specific reaction rate constant[1]

[12] Adel and Dennison, Phys. Rev. **44**, 99 (1933); **43**, 716 (1933).

[13] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

[14] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

[14a] This method of estimating the potential energy between molecules with these same percentages gives the correct activation energy for the conversion of para- to ortho-hydrogen and very close to the right activation energy in a

$$k'=\kappa\prod_{i=1}^{3}(1-\exp -h\nu_i^*/kT)^{-1}I^*I^{-1}\prod_{j=1}^{4}(1-\exp -h\nu_j/kT)(\exp -E_0/kT)kT/h \tag{3}$$

so that for the ordinary activation energy at temperature T we have

$$E=RT^2\frac{d\ln k'}{dT}=\left(\sum_{i=1}^{3}\frac{h\nu_i^*}{k}e^{-h\nu_i^*/kT}\left(1-\exp -\frac{h\nu_i^*}{kT}\right)^{-1}\right.$$
$$\left.-\sum_{j=1}^{4}\frac{h\nu_j}{k}e^{-h\nu_j/kT}\left(1-\exp -\frac{h\nu_j}{kT}\right)^{-1}+T\right)R+E^0. \tag{4}$$

This gives for $E-E_0$ at 850°, 900°, 938° and 1000°K the values 1.751, 1.799, 1.833, and 1.881 kg. cal., respectively. Thus our calculated value for E is approximately 52 kg. cal., to be compared with the measured value of Nagasako and Volmer[3b] of 53 kg. cal. Hunter[3c] agrees approximately with Nagasako and Volmer for low pressures, but he gives values ranging from 50.5 to 65 kg. cal. increasing with the pressure. He postulates three different mechanisms. We shall discuss his results later.

We are now in a position to calculate k' theoretically except for the factor κ in (3). This will also be estimated theoretically, but before doing this we determine the value to be expected from experiment. For this purpose we take $E_0=53{,}000-1.833$ cal. The moment of inertia of the activated complex, I*, is 10.14×10^{-39}, while I is 6.67×10^{-39}. The appropriate frequencies have all been given. Now taking $k'=0.00192$, the value given by Nagasako and Volmer for high pressures at 938°K, we find $\kappa=1.882\times10^{-4}$. If, instead of using this E_0 derived from Nagasako and Volmer, we use our value of 50,000 cal. we find $\kappa=3.5\times10^{-4}$.

Now Zener[2b] (see also Landau[2c]) has given the relationship

$$P_{12}=1-\exp\{-4\pi^2\epsilon_{12}^2/hv|s_1-s_2|\} \tag{5}$$

for the chance that at the point of crossing of two potential curves, such as I and II in Fig. 2, the system will jump from one curve to the other. Here v is the velocity of the system, $|s_1-s_2|$ is the absolute value of the difference of the slopes of I and II at the point of crossing. The interaction energy is $\epsilon_{12}=\int\varphi_1H'\varphi_2d\tau$ where φ_1 and φ_2 are the eigenfunctions for the two states which cross, and H' is an additional potential term (generally due to magnetic interactions) omitted from the Schrödinger equation in the approximation which gave the φ's as a solution. We find, as a result of this new term in the energy, that instead of crossing the two lower branches of I and II unite to form a single new state and the two upper branches unite to form a second new state. These two new states, instead of touching, are separated by a distance of $2\epsilon_{12}$ at the nearest point of approach, the activated state. The chief condition to be fulfilled for (5) to apply is that $\epsilon_{12}\ll\frac{1}{2}mv^2$, where m is the reduced mass of the system. In applying P_{12} to a chemical reaction we must average over-all velocities. Thus the quantity we require is

$$\bar{P}_{12}=\int_0^\infty\left(1-\exp\left\{-\frac{4\pi^2\epsilon_{12}^2m}{hp|s_1-s_2|}\right\}\right)\exp(-p^2/2mkT)dp\left(\int_0^\infty\exp(-p^2/2mkT)dp\right)^{-1}. \tag{6}$$

$\bar{P}_{12}$ is readily found by numerical integration, and if one takes $c=4\pi^2\epsilon_{12}^2m^{\frac{1}{2}}/(2kT)^{\frac{1}{2}}h|s_1-s_2|$ the values given in Table II are found for $\bar{P}_{12}$ as a function of c.

Systems in statistical equilibrium moving up along curve I in Fig. 2 have a chance $\bar{P}_{12}$ of passing to II per crossing in the forward direction.

wide variety of other cases. The very good agreement between the calculated and experimental values as given below was for this reason not unexpected.

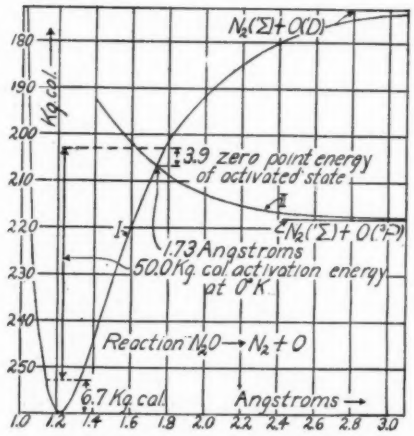

FIG. 2. Section through activated state. N_2O.

If they fail they have a second chance, $\bar{P}_{12}$, of passing to II upon their return. Thus, so long as $\bar{P}_{12}$ is small, the total chance of reaction per system passing through the activated state is $2\bar{P}_{12}$ (more exactly $2\bar{P}_{12}-\bar{P}_{12}^2$). We therefore set $2\bar{P}_{12}=\kappa$. Now $|s_1-s_2|$ from Fig. 2 is 8.50×10^{-4} ergs mol.$^{-1}$ cm^{-1}. Using the value of κ found when E_0 was taken equal to $53{,}000-1833$ cal. we find, using Table II, that $\epsilon_{12}=5.05$ cal.

TABLE II.

ϵ	1	0.1	0.01	0.001	0.0001	0.00001
$\bar{P}_{12}$	0.212	.276	.0531	.00774	.001027	.000128
ϵ	0.0^28	0.0^37	0.0^46	0.0^554	0.0^648	0.0^738	0.0^82	0.0^91
$\bar{P}_{12}$	$.0^3107$	$.0^4942$	$.0^4816$	$.0^5728$	$.0^6662$	$.0^6541$	$.0^5299$	$.0^5156$

per mole. Thus the amount, $2\epsilon_{12}=10.1$ small calories, by which the two upper branches of curves I and II fail to make contact with the corresponding lower branches is not visible on the energy scale we have chosen. Had we used our theoretical value $E_0=50{,}000$ cal., we would have found for ϵ_{12} 7.15 cal. Either of these values for ϵ_{12} fulfill the condition of being small compared with the average kinetic energy $RT/2=938$ cal. In our averaging of P_{12} we have included systems having kinetic energies equal to and lower than ϵ_{12}. This introduces some error into our calculation. However, the fraction of all particles having at the activated state a kinetic energy of ϵ_{12} and below is small, and even in this region $\bar{P}_{12}$ is approximately correct. Thus treating this region more carefully could hardly change our results by more than a few percent.

THE NATURE OF ϵ_{12}

Besides the kinetic energy of the electrons and the electrostatic potential energy of electrons and nuclei which are ordinarily considered in obtaining the energy levels which cross and which do not contribute to ϵ_{12}, we have the following types of interactions which do contribute:

(a) The relativity corrections,
(b) A perturbation associated with the kinetic energy of the nuclei,
(c) The interaction of the spin of an electron with its orbital magnetic moment,
(d) Spin-orbit interaction between two different electrons,
(e) Spin-spin interactions of the electrons inside the oxygen atom,
(f) The magnetic interaction of the spins on the nitrogen molecule with those on the oxygen,
(g) Terms responsible for the hyperfine structure.

Now all the effects except (f) involve only a single atom so their magnitudes can be estimated from atomic spectra. Of these interactions only (c) and (e) seem as large as the experimental ϵ_{12}. Condon[15] finds from experimental data that the spin-orbital interaction between O ($^1D_2$) and ($^3P_2$) is 106 cm^{-1}, or 302 small calories per mole for the isolated atom. If this value for ϵ_{12} still held at the activated state, Table II shows us that κ would be around 0.1. Actually, however, what must happen is that from both the ^1D and ^3P states of oxygen molecular orbitals are formed with no angular momentum along the molecular axis, i.e., with $\lambda=0$, while the other components of the angular momentum precess so rapidly about the molecular axis that coupling with the spin is partly destroyed. We still have spin-spin interaction inside the oxygen atom and between the nitrogen molecule and the oxygen. Of these two effects we should expect the latter to be negligible compared with the former simply on the basis of the distances between the electrons. The rough estimation of this effect of the nitrogen molecule from the point of view used by Wigner[16] in discussing ortho-para conversion indicates that we can neglect it.

The operator for spin-spin interaction is

$$\sum_{i<j}\{4\mu^2((\mathbf{S}_i\mathbf{S}_j)r_{ij}^2-3(\mathbf{S}_i\mathbf{r}_{ij})(\mathbf{S}_j\mathbf{r}_{ij}))\}/r_{ij}^5, \quad (7)$$

[15] Condon, Astrophys. J. **79**, 217 (1934).
[16] Wigner, Zeits. f. physik. Chemie **B23**, 28 (1933).

where i and j are summed over the four p electrons, giving six terms in the sum. $\mathbf{S}_i$ and $\mathbf{S}_j$ are the vectors corresponding to the angular momenta of the spins of electrons i and j, respectively, and $\mathbf{r}_{ij}$ is the vectorial distance between the electrons while r_{ij} is this distance. μ is one Bohr magneton, $eh/4\pi mc$. Now the order of magnitude of (7) is $6\mu^2\overline{r_{12}^{-3}}$. If the average of r_{12} is taken to be 1 Angstrom, we obtain 7.3 cal. per mole, the order of magnitude given by our calculations for ϵ_{12}. The theoretical treatment by Breit of spin-spin interaction in He and Li^+, taken with the experimental work of Houston and Schüler, has been presented in convenient form by Bethe[17] and indicates that the above estimate for oxygen is right as regards order of magnitude except that there is still a factor depending on the symmetry of the eigenfunctions. This factor for a singlet-triplet interaction is zero. Thus only spin-orbit interaction contributes to ϵ_{12}. A part of the smallness of κ is of course due to tunneling, which requires a corresponding revision upward of ϵ_{12}.

κ for Other Reactions Involving a Change of Multiplicity for Oxygen

If we can calculate the c defined in connection with Table II, we can obtain $\kappa = 2\bar{P}_{12}$ immediately for any reaction. The four quantities required are the reduced mass of the oxygen against the rest of the molecule being formed or decomposed, the difference of the two slopes at the point of crossing, the temperature, and ϵ_{12}. Now ϵ_{12} will be nearly the same as in N_2O so that only $|s_1 - s_2|$ offers any difficulty.

As a further example we consider the reaction $H_2+O=H_2O$ at room temperature. Bear and Eyring[18] in their Fig. 3 give, for the value of $|s_1-s_2|$, 8×10^{-3} ergs mol.$^{-1}$ cm^{-1}. $m=2.934\times10^{-24}$ g mol.$^{-1}$, $\epsilon_{12}=5.05$ cal. mole^{-1}. We take $T=300$. This gives $\kappa=1.5\times10^{-5}$.

Thus in general for a reaction involving a change in multiplicity, such as $CO+O=CO_2$, we would expect κ to be equal to 10^{-4} within a factor of about 10.

The specific reaction rate constant[1] for the reaction

$$H_2+O=H_2O \tag{8}$$

is

$$k' = \kappa \frac{i^* g^*}{i_1 i_2 g_1 g_2} \frac{(2\pi m^* kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 (8\pi^3 A^* B^* C^*)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{2h^3} \prod_{i=1}^{2} (1-\exp(-h\nu_i^*/kT))^{-1}$$
$$\cdot e^{-E_0/kT} \frac{kT}{h} \left(\frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3} \frac{(2\pi m_2 kT)^{\frac{3}{2}}}{h^3} (1-\exp(-h\nu_2/kT))^{-1} \frac{8\pi^2 I_2 kT}{2h^2} \right)^{-1}. \tag{9}$$

By neglecting the frequencies which are high this gives

$$k' = (\kappa/g_1)(m^*/m_1 m_2)^{\frac{3}{2}} h (A^* B^* C^*)^{\frac{1}{2}} I_2^{-1} e^{-E_0/kT}$$
$$= \kappa 1.83\times10^{-11} e^{-E_0/kT} \text{ cm}^3 \text{ mol.}^{-1} \text{ sec.}^{-1} \tag{10}$$
$$= \kappa 1.11\times10^{13} e^{-E_0/kT} \text{ cm}^3 \text{ mole}^{-1} \text{ sec.}^{-1} \tag{11}$$

The subscript 1 refers to 0 and 2 to H_2 and the activated complex is indicated by an asterisk. m and ν are the masses and frequencies, respectively, while i and g refer, respectively, to the statistical weights due to the nuclear spin and to the electronic states. g_1 is readily found to be 6.76 at 300°K; the product of the three moments of inertia, $(A^*B^*C^*)$, is 1.91×10^{-119} according to the dimensions given by Bear and Eyring,[18] while $I_2=4.56\times10^{-41}$. Taking $E_0=8$ kg. cal. according to these last authors, and $\kappa=1.5\times10^{-5}$, we find that k', from Eq. (11), is 269, a very slow atomic reaction. Thus oxygen atoms in the presence of hydrogen undoubtedly disappear by some mechanism other than (8), as for example $H_2+O=OH+H$, in which the multiplicity change can be avoided.

Pressure Effects in the N_2O Reaction

It is interesting to consider briefly Hunter's results[3c] on the effect of pressure on the rate of reaction. Since we may write for the specific reaction rate[19]

[17] Bethe, *Handbuch der Physik*, Vol. 24, No. 1 (Berlin, Julius Springer, 1933).

[18] Bear and Eyring, J. Am. Chem. Soc. **56**, 2020 (1934).

[19] Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935).

$$k' = K^* \frac{kT}{h} = \exp -\frac{[\Delta E^* + \Delta(pV)^*]}{RT} \exp\left[\frac{\Delta S^*}{R}\right] \frac{kT}{h} \tag{12}$$

we may, of course, apply the usual thermodynamic considerations. Evans and Polanyi[20] have discussed the effect of pressure on reaction rates from a similar point of view. The process of taking partial derivatives gives

$$\left(\frac{\partial \log k}{\partial T}\right)_V = \left(\frac{\partial \log k}{\partial T}\right)_p - \left(\frac{\partial \log k}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p . \tag{13}$$

Because of a misprint in their article they have a positive sign before the last term in (13). This does not affect their final results since, of course $(\partial p/\partial V)_T$ is a negative quantity so that they find

$$((d \log k)/dT)_V \geqq 1.12((\partial \log k)/\partial T)_p \tag{14}$$

for the reaction

$$C_5H_5N + C_2H_5I = C_5H_5N\begin{matrix} \diagup I \\ \diagdown C_2H_5 \end{matrix}$$

in acetone. Now Hunter measured $((\partial \log k)/\partial T)_p$, so that we cannot invoke (12) to explain his high activation energies as we might had he measured $((\partial \log k)/\partial T)_V$.

There is still another pressure effect also considered by Evans and Polanyi. From (12) we obtain at once

$$\left(\frac{d \log k'}{dT}\right)_p = \frac{\Delta H^* + RT}{RT^2} = \frac{\Delta E^* + RT}{RT^2} + \frac{p\Delta V^*}{RT^2} . \tag{15}$$

We assume that the N_2O molecule excludes other molecules from a prolate spheroid formed by the rotation of an ellipse about the molecule's major axis $a = b + r_3$ where b is the minor axis and r_3, as before, is the distance between the O and the far nitrogen atom. This volume is then $(\pi/6)(b + r_3)b^2$. Now the molal volume of liquid N_2O is 36 cc, and $r_3 = 2.32$A in the normal molecule so that we have $b = 4.16$A. Thus by increasing r_3 to 2.83A, as in the activated state, the molal volume is increased by only 2.8 cc. Consequently at a pressure of 40 atmospheres the quantity $p\Delta V$ increases the activation energy by only 2.7 small calories. We must therefore conclude that if Hunter's interpretation of his experimental results is correct, then at high pressures the decomposition goes by some new mechanism, as he suggests.

Although the picture of the nonadiabatic unimolecular decomposition of N_2O at moderate pressures with an activation energy of approximately 53,000 calories seems very satisfactory, an explanation of Hunter's high pressure results is not given.

We wish to take this opportunity of expressing our appreciation to Dr. Wendell Jackson for joint consideration of some of the initial phases of this problem, and also to Dr. G. E. Kimball for helpful discussions.

[20] Evans and Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

The Absolute Rate of Homogeneous Atomic Reactions

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(Received September 4, 1935)

The absolute rate of the recombination of three hydrogen atoms is calculated entirely theoretically. The manner in which rotation determines the dimensions of the activated complex in cases having little or no activation energy is discussed. The theoretical data are in good agreement with the experimental rates of Steiner and of Amdur. An immediate consequence of the theory is that energy transfer occurs most effectively among particles which can react with each other, free atoms being more efficient than molecules. A qualitative application of potential surfaces to the problem of energy transfer as met in velocity of sound experiments and in experiments on maintenance of high pressure rates of unimolecular reactions is made.

INTRODUCTION

IN previous papers[2] there has been developed and applied a theory of the rates of homogeneous reactions which takes explicitly into account the behavior of all the degrees of freedom of the reacting system. In order to evaluate exactly the expressions that are obtained it is necessary to construct a potential energy surface for the system. In the applications that have already been made[2(b, c)] this was not feasible and it was necessary to obtain approximate information about the surface from the data of spectroscopy. For diatomic and triatomic systems, however, it is possible to construct a surface which is in agreement with experimental data.[3] In this paper we shall show that from such surfaces one can calculate rates of reaction agreeing with experiment. From the surfaces considerable information is obtained concerning the mechanism by which energy is transferred during the three-body collisions by which atomic recombinations take place.

We shall consider in detail the reaction $H+H+X\rightarrow H_2+X$. Before proceeding to this case, we first consider atomic reactions of the type $A+B\rightarrow AB$. Although this reaction is very improbable, it is of great interest because from an investigation of the properties of the potential surface one learns how to take into account the relative angular momentum of two bodies which are going to react and also what is meant by the collision diameter for such a reaction. This information can be carried over to associations of diatomic or polyatomic molecules in which there is no activation energy.

These results are of interest also in connection with the important work of Pelzer and Wigner[4] who took less explicit account of the fact that molecules usually approach with relative angular momentum.

THE REACTION $AB\rightarrow A+B$

The general equation for the rate of any reaction is[5]

$$k_i=\kappa(F_a'/F_n)(kT/h)e^{-E_0/RT}. \qquad (1)$$

This equation gives the concentration of the systems at a saddle point on the surface times the rate at which they are crossing the barrier times the probability (κ) that once they cross the barrier they do not recross it. The usual potential energy surface for two atoms (Morse curve) is two-dimensional and it has no saddle point (maximum) except at infinity. It would seem as if Eq. (1), therefore, could not be applied. We must, however, remember that the Morse curve gives the energy of a system of two atoms as a function of the distance between them only for the case in which the atoms are approaching along the same straight line. In general this situation will not be encountered;

[1] Parker Traveling Fellow of Harvard University, 1934–5.

[2] (a) Eyring, J. Chem. Phys. **3**, 107 (1935). (b) Gershinowitz and Eyring, J. Am. Chem. Soc. **57**, 985 (1935). (c) Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935).

[3] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

[4] (a) Pelzer and Wigner Zeits. f. physik. Chemie **B15**, 445 (1932). (b) Pelzer, Zeits. f. Electrochemie **39**, 608 (1933). (c) Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).

[5] Reference 2(a) Eq. (10). In accordance with the notation used in reference 2(c), κ has been substituted for c, the transmission coefficient, in order to avoid confusion with concentration.

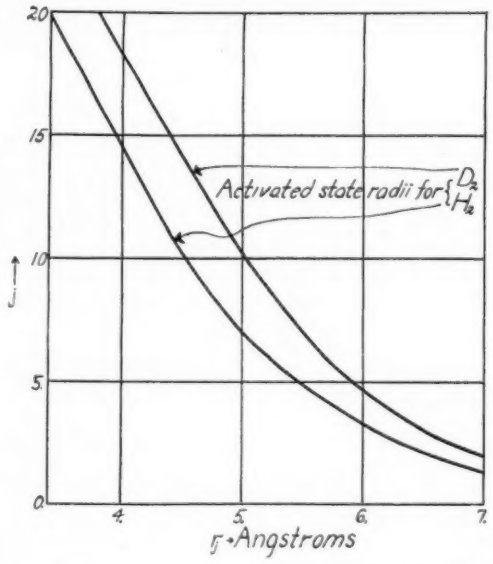

FIG. 1. The distance between the atoms in the activated state in the bimolecular association of H_2 and D_2.

the atoms will have a relative angular momentum, which may be considered as a rotation in two degrees of freedom. The kinetic energy of rotation for each quantum state and for each interatomic distance must be added to the potential energy arising from electronic interaction, the latter being given by the Morse curve. The sum gives the energy that must be used in the exponential of the partition function, if we take as our zero of energy, for both the activated and normal states, the energy of the nonrotating molecule in its lowest vibrational state. For the case of two atoms we then have the activation energy E_0 equal to D, the energy of dissociation. Now the addition of the energy of rotation to the rest of the energy of the molecule will cause a shift in the position of the activated state. For the dissociation of a diatomic molecule with no rotation there is no maximum, so that the activated state is at infinity. When we have a rotating molecule we do get a maximum and as the energy of rotation increases the distance r_j at which the maximum occurs becomes smaller. (See Fig. 1. These curves have meaning only for the integral values of J, the rotational quantum number.)

This maximum locates the position of the activated state for the corresponding value of the rotational quantum number J. Knowing this we may calculate the activation energy for each value of J and by summing over all J's we obtain the rotational partition function. Because of the Boltzmann factor, rotational states of very high energy are weighted out, so that at each temperature, for the association of two atoms there is an apparent collision diameter not very different from that for the collision of two diatomic molecules of the same kind. By differentiating with respect to r the total energy $E=E_{\text{vib}}+E_{\text{rot}}$ for each value of J and setting this derivative equal to zero, we find r_j, the separation between the atoms in the activated state for the corresponding rotational quantum number. Fig. 1 gives the plot of r_j against J for H_2 and D_2 at 300°K.

The activated state for the dissociation of a diatomic molecule thus lies at the top of a different maximum for each value of J. For the specific rate k_1 of the reaction

$$AB \rightarrow A \cdots B \rightarrow A+B$$

we then have:

$$k_i=\frac{g_a i_a \kappa (2\pi(m_1+m_2)kT)^{\frac{1}{2}}h^{-3}\sigma_a^{-1}\sum_{J=0}^{\infty}(2J+1)\exp\{-(J(J+1)h^2(8\pi^2\mu r_j^2)^{-1}-(D-E_V))(kT)^{-1}\}kTh^{-1}\exp\{-D(kT)^{-1}\}}{g_n i_n (2\pi(m_1+m_2)kT)^{\frac{1}{2}}h^{-3}(1-\exp\{-h\nu(kT)^{-1}\}\sigma_n^{-1})\sum_{J=0}^{\infty}(2J+1)\exp\{-J(J+1)h^2(8\pi^2\mu r_0^2 kT)^{-1}\}} \quad (2)$$

$=LM^{-1}$ where L and M are the numerator and denominator, respectively, of the preceding fraction. For the reverse reaction

$$k_2=L\{(2\pi m_1 kT)^{\frac{1}{2}}h^{-3}(2\pi m_2 kT)^{\frac{1}{2}}h^{-3}g_m i_m\}^{-1}. \quad (3)$$

κ is the transmission coefficient, i.e., the fraction of systems which, having crossed the maximum, do not return, m_1 and m_2 are the masses of the atoms in the molecule; $\mu=m_1m_2/(m_1+m_2)$; σ_a and σ_n are the symmetry numbers

of the activated and normal states, respectively. ν is the vibration frequency of the molecule. i_a, i_n and i_m are the statistical weights due to nuclear spins and remain equal since ortho and para forms are always present in equilibrium amounts; however, for the statistical weights of electronic states we have $g_a=g_n=1$ and $g_m=4$.

The zero of energy is chosen to correspond to the nonrotating molecule in its lowest vibrational state; hence D is the energy of dissociation from this level to the asymptote of the Morse curve. E_V is the energy of vibration measured from the lowest vibrational state as taken from the Morse curve at the activated point r_j for each J. The rotational term in the denominator of (2) involves the constant r_0, the equilibrium separation of the atoms in the normal molecule, so that this moment of inertia is not a function of J. (We neglect the small interaction of vibration and rotation.) Thus at reasonably high temperatures we can replace this summation by $8\pi^2\mu r_0^2kT(\sigma_n h^2)^{-1}$. The rotational partition functions for the normal and activated states of H_2 and D_2 at 500°K are given with considerable accuracy by the areas under the appropriate curves of Fig. 2. (The true curves are steplike.) The maxima of these curves give the most probable J's for this temperature. With these most probable J values we can calculate the most probable values of $\bar{r}_j$ (the collision diameter). A more useful average $\bar{\bar{r}}_j$ can be obtained from the equation

$$8\pi^2u\overline{\overline{r_j^2}}kTh^{-2}=\sum_{j=0}^{\infty}(2J+1)\exp-\{(J(J+1)h^2(8\pi^2ur_j^2)^{-1}-(V-E_V))(kT)^{-1}\}. \quad (4)$$

We find that for hydrogen $\bar{\bar{r}}_j=4.4$A and $\bar{r}_j=4.8$A; for deuterium $\bar{\bar{r}}_j=4.1$A and $\bar{r}_j=4.9$A. For Cl_2 and Br_2 one gets r_j's of the same order of magnitude. In general, if the association of two particles, atoms or radicals, requires no activation energy the apparent collision diameter, corresponding to the dimensions of the activated state, will be determined by the relative angular momentum, and at room temperature will be from 4 to 5A. We have applied this generalization in our treatment of trimolecular reactions.[2b]

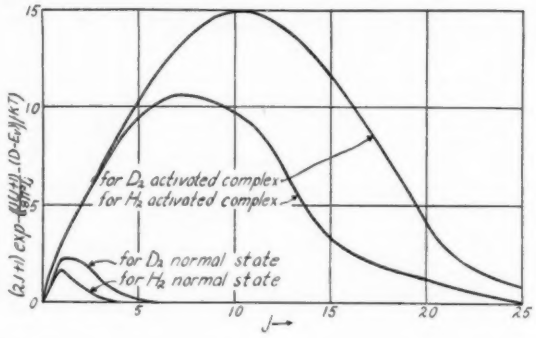

FIG. 2. Weighted number of states for each value of J. In normal state $D=E_v$. (Bimolecular association.)

From Eqs. (2a) and (2b) we can now calculate the rates of bimolecular association and unimolecular decomposition of H_2 and D_2. If we assume that κ is the same for the reaction of D_2 and H_2 for H_2 we find

$$k_1=\kappa 3.6\times10^{14}e^{-D/RT}\ \text{sec.}^{-1},$$
$$k_2=\kappa 2.78\times10^{14}\ \text{cm}^3\ \text{moles}^{-1}\ \text{sec.}^{-1},$$

and for D_2

$$k_1=\kappa 3.61\times10^{14}e^{-D/RT}\ \text{sec.}^{-1},$$
$$k_2=\kappa 1.99\times10^{14}\ \text{cm}^3\ \text{moles}^{-1}\ \text{sec.}^{-1}.$$

The transmission coefficient κ is something like 10^{-14} instead of being of the order unity as it frequently is when no non-adiabatic process is involved.[6]

We see that H_2 and D_2 decompose unimolecularly at the same rate except for the difference in zero-point energy. This is because the mass factors cancel out in the general equation for the rate and in addition the ratio $F^*_{\text{rot}}/F_{\text{rot}}$ is the same for H_2 and D_2 although the individual rotational partition functions for the activated and normal states (F^*_{rot} and F_{rot}) for H_2 are quite different from those for D_2. We also note that the rate k_2 for the unimolecular association of hydrogen atoms is nearly $(2)^{\frac{1}{2}}$ times the rate of association of deuterium. This is to some extent fortuitous, since it arises from the cancelation of a number of terms. This ratio of $2^{\frac{1}{2}}$ for the relative rates strikingly exemplifies the

[6] For an excited diatomic oscillator with a reasonable sized dipole the interval before radiation is frequently around 10^{-2} sec. In the case of hydrogen, where there is no dipole but only a quadrupole moment, we should expect a mean life of the order of seconds, so that κ may well be as small as $1/\nu\approx10^{-14}$.

fact that one is not justified in postulating simple mechanisms or rate expressions on the basis of a single numerical agreement.

The reason that the bimolecular association of the atoms plays a negligible role in the actual process of recombination is that κ is so very small. The usual assumption will be shown to be correct that at atmospheric pressure about every thousandth collision among atoms is a three body one and forms a stable molecule whereas only about every 10^{-14} diatomic collision is stabilized by radiating energy.

The Reaction $A+B+C \rightarrow AB+C$

We first consider the case in which A, B and C are all hydrogen atoms. A system of three atoms has nine degrees of freedom. In the normal state all these are free translations. In the activated state we have a triatomic quasimolecule. For three hydrogen atoms for all except very large distances the configuration of lowest potential energy is that in which all three atoms lie on the same straight line. This important type we discuss first. The other important type to be treated later is the isosceles triangle configuration for the activated complex. The nine normal coordinates of the linear complex are three of translation of the system as a whole, two of rotation of the system, two for bending vibrations and two for motions along the straight line. We make the usual assumption that the two rotations and three translations are separable from the four internal coordinates. Of the four internal coordinates there are two transverse vibrations of equal frequency. Upon writing out in full the potential energy for the system the two transverse vibrations are seen to be separable from the two motions along a straight line up to terms involving the fourth power of the bending angle. Because this interaction is so small it is principally the transfer of energy between the two remaining degrees of freedom which is responsible for the stabilization (or dissociation) of the diatomic molecule by the third body. These last two degrees of freedom then are those which we now investigate.

Eyring and Polanyi[3] in collaboration with Wigner have shown how to construct a potential energy surface for three collinear atoms such that the classical motion of a mass point on this surface will describe the behavior of the system. Such a surface for 3H atoms is shown in Fig. 3. r_1 represents the distance between atoms 1 and 2 and r_2 the distance between atoms 2 and 3. The contour lines are equipotentials spaced at intervals of 5 kg.cal. Both Figs. 3 and 4 were constructed in the usual way[3] with 14 percent Coulombic energy and the following constants for the Morse curve for hydrogen: heat of dissociation = 102.4 kg.cal.; vibration frequency $\omega_0 = 4375$ cm^{-1}; $a = 1.94A^{-1}$; $r_0 = 0.74A$. This surface has many features in common with other surfaces which represent the interactions of three atoms, any two of which can form a diatomic molecule. The angle that the axes make with each other is always 60° for three like atoms; otherwise it is a function of the relative masses.[3] For any set of three atoms the surface will have the same general appearance. In particular, for the regions of high potential energy, in which we shall be principally interested, the surfaces are divided by some line into two regions, each of which is developable, i.e., the energy in each may be expressed as the sum of two potentials each depending on a single coordinate.[7] It is this feature which enables us to discuss simply the transfer of energy between the two degrees of freedom associated with the two distances r_1 and r_2 and to determine the probability that a system with a given amount of energy will react. These two degrees of freedom of the linear molecule fix the relative translation of the three atoms. In what follows, for the sake of definiteness, we shall refer to the hydrogen surface shown in Fig. 3 in which the dividing line is $r_1 = r_2$. The behavior of other systems of three atoms which can form diatomic molecules is entirely analogous. The cases in which one of the atoms is an inert gas or in which the catalyzing particle is a molecule will be discussed later.

Although the surface is somewhat approximate in the region of low potential energy it is much more accurate for energies greater than 45 kg.cal.

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[7] See for example Kimball and Eyring, J. Am. Chem. Soc. **54**, 3381, etc. (1932) Figs. 1, 2, and 3 in which this feature is to be observed. In these particular cases, as well as for the three hydrogen atoms, the line makes equal angles with the coordinates r_1 and r_2.

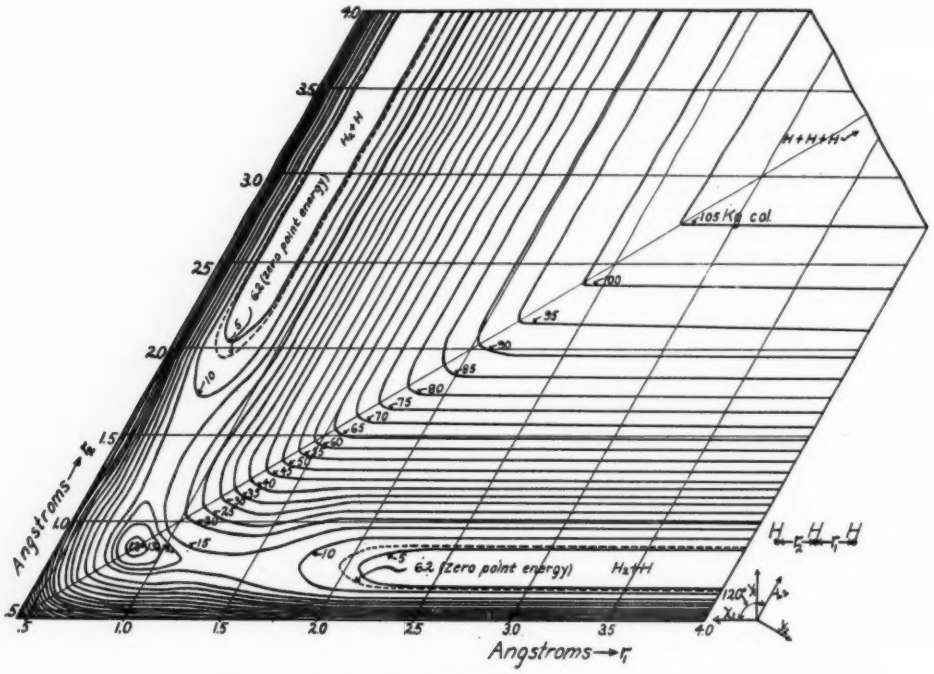

FIG. 3. Energy contour map of linear H_3 molecule.

per mole. We shall see that the greater part of the systems that associate (or dissociate) cross the line $r_1=r_2$ in the region of high potential energy, so that the part of the surface that is inexact does not enter into our calculations. The calculations in the section immediately following depend only on that portion of the surface corresponding to potential energies greater than 45 kg.cal.

The section of the surface to the right of the line $r_1=r_2$ is developable in terms of the Cartesian coordinates x_1 and y_1. The part to the left and above $r_1=r_2$ is developable in terms of the Cartesian coordinates x_2 and y_2, the latter of which is taken perpendicular to the axis r_2. The angle between y_1 and y_2 and between x_1 and x_2 is then 120° (see Fig. 3). The energy of the mass point representing the system when it is in the first region is

$$\tfrac{1}{2}u(\dot{x}_1^2+\dot{y}_1^2)+V(x_1, y_1), \tag{5}$$

where $\dot{x}=\dfrac{dx}{dt}$ etc.; $u=\dfrac{(m_1+m_2)m_3}{m_1+m_2+m_3}=\dfrac{2}{3}m$

for our hydrogen atoms.[8] Similarly, in the upper part of the surface the energy is

$$\tfrac{1}{2}u(\dot{x}_2^2+\dot{y}_2^2)+V(x_2, y_2).$$

Along the line $r_1=r_2$ we have the relation

$$y_2=0.5y_1+0.866x_1. \tag{6}$$

This relation expresses the physical fact that suddenly as r_1 becomes equal to r_2 motion within the system which was pure translation becomes redistributed between vibration and translation. This redistribution also takes place in the vibrational energy. This abrupt change in developability in one set of coordinates to developability in another probably often holds in ordinary molecules where there is no internal translation. Where this is found to be so it will provide a very convenient means of discussing many problems. Let us now suppose that in the x_1, y_1 valley

[8] See Eyring and Polanyi, reference 3. Fig. 16 and accompanying text. Their coordinates $-b$ and g correspond to our x_1 and y_1. We should also like to mention that in their Eq. (25) on p. 307 sin φ should be replaced by $-$ sin φ. Accordingly, the angle between b and c in Fig. 17 should be taken as 60°, as we have done in our Fig. 3, where r_1 and r_2 correspond to b and c, respectively. We are indebted to Dr. O. K. Rice for kindly pointing out this error in sign.

there is a system (mass point) whose total energy is greater than $108.6+R(J)$ kg.cal., where $R(J)$ is the rotational energy corresponding to the angular momentum of the entire system. (This $R(J)$ creates a ridge along the edge of the valleys converting the central plateau into a shallow basin, in the same manner as it forms the maximum of the potential energy curve for the diatomic molecules, which case we have discussed above.) If the point representing our system is to remain in the valley (in spite of having the energy $108.6+R(j)$, which is enough to dissociate it), this energy must be distributed in the x_1 and y_1 directions in such a way that the part of it in the y_1 direction, $\frac{1}{2}m\dot{y}_1^2+V(x_1, y_1)$, is less than $108.6+R(J)$ kg.cal. Since the surface is developable in this region we can have no transfer of energy between the x_1 and y_1 directions, so that the system cannot dissociate before it reaches the median line. When the mass point reaches this line it will pass into the other valley, since along the part of this line where $V(r_1, r_2)=45$ kg.cal. (which is the region we are considering) no activation energy is needed, as the surface shows. As soon as it crosses this line the energy will be developable in terms of the coordinates x_2, y_2, $\dot{x}_2$ and $\dot{y}_2$ where $\dot{y}_2$ is given by Eq. (6). We see, therefore, that there is a definite probability that enough energy will be transferred to the y_2 direction to make the system dissociate, i.e., cross over the ridge of the valley onto the plateau and remain there. By the principle of microscopic reversibility, this will also give us the probability that a system of three atoms will react to give a molecule and an atom. This is the reverse reaction in which we are, of course, also interested.

There remains only the formal problem of setting up the required probability integral. We first consider

$$H=h^{-2}\int_a^b dx\int_c^d dy\int_e^f dp_x\int_k^l dp_y \exp -\{(\tfrac{1}{2}u(\dot{x}_1^2+\dot{y}_1^2+V(x, y))(kT)^{-1}\}, \tag{7}$$

where h^{-2} is the normalization factor. We determine the limits a, b, c, etc., in the following manner. We are interested in the fraction of systems for which

$$\tfrac{1}{2}u(\dot{x}_1^2+\dot{y}_1^2)+V(x_1, y_1)>108.6+R \tag{8}$$

and at the same time

$$\tfrac{1}{2}u\dot{y}_2^2+V(x_1, y_1)>108.6+R, \tag{9a}$$

which, by (6), becomes

$$\tfrac{1}{2}u(0.5\dot{y}_1+0.866\dot{x}_1)^2+V(x_1, y_1)>108.6+R. \tag{9b}$$

There are the additional conditions

$$0<\dot{x}_1<\infty \tag{10}$$

and

$$0<\tfrac{1}{2}u\dot{y}_1^2+V(x_1, y_1)<108.6+R, \tag{11}$$

which restrict the systems considered to the valley. These four conditions taken together restrict us to the fraction of systems originally composed of a molecule and an atom in the x_1, y_1 valley which dissociate into three atoms after crossing into the x_2, y_2 valley. These conditions give the upper and lower limits of the probability integral H. The two strongest conditions are (9b) and the second inequality in (11) which we will call (11b). (11b) gives the upper limit for $_1\dot{y}$

$$\dot{y}_1=(2(108.6+R-V))^{\frac{1}{2}}u^{-\frac{1}{2}}=g.$$

From (9b) we can obtain the lower limit for $\dot{y}_1$; for, solving, we get

$$\dot{y}_1=2g-1.732x_1=2g-3^{\frac{1}{2}}g.$$

But this is the lower limit only until $\dot{y}_1=-g$, otherwise condition (11b) would not be fulfilled. Letting $\dot{y}_1=-g$ and solving for $\dot{x}_1$, we get $\dot{x}_1=3^{\frac{1}{2}}g$. There is also a lower limit on $\dot{x}_1$, since $\dot{y}_1$ cannot be greater than g, i.e., $\dot{x}_1=g3^{-\frac{1}{2}}$. We can, therefore, divide our space into two regions, in one of which

$$2g-3^{\frac{1}{2}}x_1\leq\dot{y}_1\leq g \quad\text{and}\quad g3^{-\frac{1}{2}}\leq\dot{x}_1\leq 3^{\frac{1}{2}}g; \tag{I}$$

and in the other

$$-g\leq\dot{y}_1\leq g \quad\text{and}\quad 3^{\frac{1}{2}}g\leq\dot{x}_1\leq\infty. \tag{II}$$

If we replace the coordinates x and y by the coordinates ξ measured along the line $r_1=r_2$ and η perpendicular to this direction, our potential at the activated state can be written as a function of ξ alone, to a good approximation. The rate with which the reaction proceeds is given by the density in phase space of the points representing

the reacting system per unit of length normal to the line $r_1=r_2$ multiplied by the velocity of these points in the η direction. Since we can neglect the small dependence of the potential upon η the integral over unit length $\int_{-\frac{1}{2}}^{\frac{1}{2}}d\eta$ simply yields unity. The limits of the integral over ξ as well as the potential along this line $r_1=r_2$ are dependent on the amount of rotation and therefore upon the quantum number J for this linear symmetrical activated complex. For $J=0$ corresponding to no rotation an interesting situation arises. To get the number of molecules formed we should integrate ξ from $r_1=r_2=0$ to $r_1=r_2=l$ where l is of the order of a mean free path, since at this distance the attractive potential will have a maximum due to external perturbations. Actually if all such collisions resulted finally in the formation of a stable molecule we should get a very large rate of combination. We must, however, consider the subsequent fate of the diatomic molecule formed with such a very large amplitude of vibration, i.e., the corresponding κ. A subsequent collision normal to this axis will almost certainly decompose the molecule whereas a collision in the direction of the axis is apt to stabilize it. Thus the chance that the molecule will persist after the next collision is approximately d/l where d is a normal atomic collision diameter and l is the length of the molecular axis (the mean free path). We should, therefore, (when $J=0$ as for other cases) use approximately d rather than the mean free path l as the upper limit in the phase integral (7) (if κ is to be taken as approximately unity) since this integral is very nearly proportional to the upper limit.

Now instead of considering the surface for each value of J separately we use the surface for $J=0$ and integrate out to $r_1=r_2=4.4$A which is the position of the rotation ridge separating the plateau from the valley for the average J at this temperature (300°A). This procedure introduces but little error since the potential surfaces change only slightly with J and even choosing the position of the rotation ridge 1A too far out would only multiply the true rate by a factor of approximately 1.25. Underestimating the distance to the ridge by a similar amount underestimates the rate by a similar factor.

Introducing the limits of integration into (7) gives the equality

$$H=h^{-2}\int_0^{4.4\times 3^{\frac{1}{2}}}\exp-\{V(\xi)(kT)^{-1}\}d\xi\left[\int_{\dot{x}=\dot{y}3^{-\frac{1}{2}}}^{3^{\frac{1}{2}}\dot{y}}\int_{-2\dot{y}-x3^{\frac{1}{2}}}^{\dot{y}}\exp-\{\tfrac{1}{2}\mu(\dot{x}^2+\dot{y}^2)(kT)^{-1}\}\mu^2d\dot{x}d\dot{y}\right.$$
$$\left.+\int_{\dot{x}=\dot{y}3^{\frac{1}{2}}}^{\infty}\int_{-\dot{y}}^{\dot{y}}\exp-\{\tfrac{1}{2}\mu(\dot{x}^2+\dot{y}^2)(kT)^{-1}\}\mu^2d\dot{x}d\dot{y}\right].$$

We have evaluated this integral numerically. The region fo which $V(\xi)$ is less than 45 kg.cal. makes a negligible contribution. Even keeping the original assumption that the surface is ruled, the contribution along the line $r_1=r_2$ near the minimum is unimportant. Now the fact that the minimum is higher than corresponds to such an assumption decreases still further the contribution to H from this region since it introduces an activation energy for particles crossing $r_1=r_2$ near the minimum. We estimate the error made by neglecting the region where $V(\xi)<45$ kg.cal. to be not more than 10 percent. If we take for the zero the energy of three separated hydrogen atoms we find that $H=2\mu kT\cdot 1.64\times 10^{-8}/h^2$. It can be shown that if all systems crossing the line $r_1=r_2$ with enough energy actually reacted, the corresponding partition function H' would be equal to $2\pi\mu kT\cdot 4.4\times 10^{-8}/h^2$. The ratio H/H' gives us a measure of the transmission coefficient κ. We find that approximately $\frac{1}{8}$ of the systems that cross the barrier with enough energy react. In this case there is only one degree of freedom which can take away the excess energy. Where there are more, κ will be larger, and for polyatomic molecules it will approach unity.

The rate of the association reaction k_3 is therefore given by

$$k_3=\frac{g_a i_a}{g_n i_n}\frac{8\pi^2 I^* kT(\sigma^* h^2)^{-1}\prod_{i=1}^{2}(1-\exp-\{h\nu_i(kT)^{-1}\})^{-1}(2\pi m^* kT)^{\frac{1}{2}}h^{-3}H\bar{v}}{(2\pi mkT)^{9/2}h^{-9}}, \tag{12}$$

where I^*, σ^*, $\bar{v}=(kT/2\pi m^*)^{\frac{1}{2}}$ and ν_i are, respectively, the moment of inertia, symmetry number, average velocity across the barrier and vibration frequencies of the activated complex; m is the mass of one of the atoms. $g_a i_a (g_n i_n)^{-1}=\frac{1}{4}$ exactly as for the bimolecular association. In this expression the most uncertain quantity is the moment of inertia of the activated complex, since the atoms may be from two to four Angstroms apart when they cross the line $r_1=r_2$, and the distance l is also a function of J. We take as an average, as well as a most probable value, $r_1=3$A. This makes our maximum error a factor of two, although the probable error is much less. The one other uncertain quantity is the magnitude of the frequencies of the transverse vibrations. The absolute rate is not very sensitive to changes in this quantity, but without it we cannot predict the isotope effect with H_2 and D_2. The evidence available seems to indicate that these frequencies should be somewhat lower than those given by surface IV. If we assume the frequencies are very low the vibration partition functions take the classical values $kT/h\nu_i = kT2\pi m^{\frac{1}{2}}/hf_i^{\frac{1}{2}}$ and we get a factor of m from the two frequencies of the activated state. This m in the numerator with the $m^{\frac{1}{2}}$ in the denominator of (9) gives an $m^{-\frac{1}{2}}$ as the final dependence of the rate on the mass. This agrees with the results of Farkas[9] and with those of Amdur.[10] This agreement gives us some information about the values of the vibration frequencies that we must insert into Eq. (12). To give the classical mass dependence these frequencies must be of the order of magnitude of 100 cm^{-1}. Using this frequency we get 7 as the numerical value of the partition function for the two transverse vibrations. Although the bending frequencies are low the one associated with ξ is sufficiently large to make the total zero-point energy approximately that of the normal state in agreement with the results of Farkas and of Cook and Bates.[9] Substituting in (12) the numerical values, we get $k_3=3.1\times10^{15}$ cm^6 $moles^{-2}$ $sec.^{-1}$.

The process just considered involves the three atoms 1, 2 and 3, where 2 lies in between. Atom 3 comes up to the unstable configuration 1–2, atom 1 leaves and 2 and 3 form a stable molecule. This mechanism accounts for those cases in which the atoms are moving along a straight line, or at such angles as are included by the amplitudes of the transverse vibrations of our activated state. When the amplitudes of these vibrations are very large, i.e., for atoms approaching at very sharp angles, it is no longer legitimate to make the assumption that the energy is still separable in terms of the coordinates that were good approximations to normal coordinates for the linear case. This being so it may be there is some second region of our many dimensional energy surface which is as effective as that just considered. Such a new region would make possible an additional mechanism for the reaction. We find that this situation actually arises for configurations in which one of the three atoms is moving perpendicular to the line forming the other two. The pair moving along the line reacts and the third carries off (or for the reverse process furnishes) the excess energy.

Second Type of Collision for 3 H Atoms

Fig. 4 is the potential energy surface for two hydrogen atoms moving along a straight line, the distance between them being r_1 with the third hydrogen atom moving perpendicular to and toward (or away from) the center of this line. The distance from the third atom to the center of gravity of the first two is r_2. The three atoms thus always form an isosceles triangle. In Fig. 4 only a little more than half the surface is drawn as it is symmetrical about $X=0$. Here again we see that a line AB divides the surface into two regions in which different sets of coordinates are appropriate. In the region to the southeast of AB the most convenient coordinates are the parabolic cylindrical set,[11] u, v and w, where

$$x=c(v-u); \qquad y=2c(uv)^{\frac{1}{2}}; \qquad z=w.$$

In this coordinate system our equipotential lines are nearly the parabolas $v=$const. In the region to the northwest plane polar coordinates ρ and θ with origin at the point c may be used and in this part of the surface the equipotentials are given to a good approximation by $\rho=$const.

[9] Private communication.
[10] Amdur, J. Am. Chem. Soc. 57, 856 (1935).
[11] Adams, *Smithsonian Mathematical Formulae* (1922), p. 105.

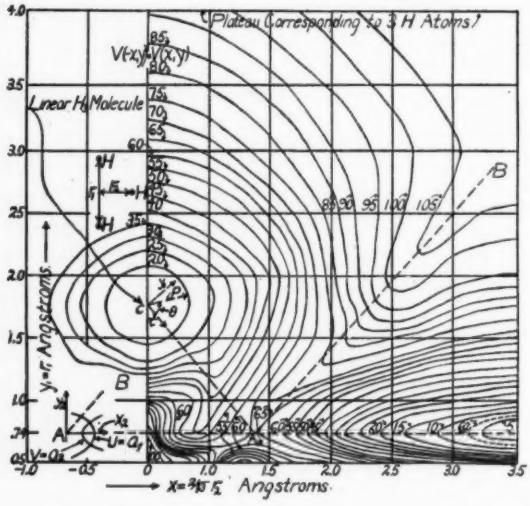

FIG. 4. Energy contours at 5 kg.cal. intervals for 3 H atoms forming isosceles triangle.

In these regions the surfaces are not developable, i.e., there is transfer of energy between the u and v directions and between the ρ and θ directions. However, because of the general shape of the surface in the neighborhood of the line AB we can treat it as consisting of two valleys intersecting at an angle of 130° by the same method as was used for the two valleys meeting at 60° in Fig. 3. From this point of view this type of collision is seen to be less efficient than the linear one first because the angle differs more from the most favorable angle of 90° and secondly because the height of 65 kg.cal. for the minimum in the pass has the effect of excluding many more colliding systems than did the former 15 kg.cal. height. Therefore, this type of collision cannot as much as double our calculated rate.

We have, then, that, within a factor of two or three, the calculated rate of recombination of hydrogen atoms is 3.1×10^{15}, as compared with the experimental results of Amdur[10] and of Steiner[12] of 2×10^{16} and 1×10^{16}, respectively.

CASES WHEN THE THIRD PARTICLE IS NOT AN H ATOM

For definiteness we discuss the case when the third atom is helium and take the distance from He to the nearest H as r_2. A new map will not be drawn. Instead the differences will be indicated by reference to Fig. 3. The surface instead of having an angle of 60° between the r_1 and r_2 direction now has 50° 46′. The effective mass of the point representing the system instead of being half the mass is now 4/3 the mass of a hydrogen atom and distances in the r_2 direction must be multiplied by $(\frac{5}{8})^{\frac{1}{2}}$ before plotting.[3] Because unexcited He cannot form a valence compound with the H atom the lower valley of Fig. 3 disappears. Instead we have only a very shallow van der Waals valley at a considerably larger value of r_2 (around 3.75A). For smaller values of r_2 the surface rises rapidly. Van der Waals attraction is of course present in the case of 3 H atoms but is unimportant compared with the valence valleys and so was not discussed. From the nature of this new surface it is clear that neither helium nor any other inert molecule can approach an H atom in efficiency of carrying away energy in a linear collision, since so much of the region which contributes to the reaction of 3 H's is here shut off by a high hill, and since for the available region entrance of the mass point into the valley is necessarily at a less favorable angle.

We now consider the case corresponding to Fig. 4 in which the inert gas approaches the center of gravity of the combining atoms normal to the molecular axis. The circular region about c now becomes a peak instead. If a particle is to leave the plateau and remain in the valley it must roll into the valley on the end formed by the peak. This is only possible if the relative velocities in the r_1 and r_2 directions lie within narrow limits and if the point is directed at the peak in just the right way. However, these requirements are not quite as stringent as for the linear case, i.e., the limits of integration in the integral H not quite as narrow. This is because the barrier across the valley formed by the peak leaves it more accessible from the plateau than in the linear case. Given the surface it is of course a straightforward problem in statistical mechanics to calculate the specific rate for this process. This qualitative discussion of surfaces shows in an unambiguous way how the increased accessibility of the end of the valley

[12] Steiner, Trans. Faraday Soc. **31**, 623 (1935).

to the plateau (which is associated with increasing reactivity) increases the transfer of energy between degrees of freedom.

Comparison with Experimental Results

There is some disagreement as to the relative efficiencies of H and H_2 as third bodies in the recombination of hydrogen atoms. The work of Steiner indicates that H_2 is at least ten times as efficient. The work of Amdur gives contrary results. We can examine these relative efficiencies from the theoretical point of view which we have adopted. In order to have a hydrogen molecule transfer energy by an exchange of partners, it must lie between two atoms on a straight line. Thus we have the configuration H—H–H—H and reaction will occur when the central hydrogen molecule splits and we get two new ones formed. There are three factors which might make this process less probable than the reaction with three hydrogen atoms. The first is that there is less probability of finding the four atoms on a line than of finding three. The difference, however, is not as great as one might expect, for the rotational partition function of hydrogen is so small that the molecules will have the correct orientation about half the time. Secondly, one-third of those collisions in which the atoms are collinear will have the molecule between the two atoms. These combined probabilities would make the hydrogen molecule $\frac{1}{6}$ as effective as the atom. The third factor that could reduce the efficiency would be the necessity of an activation energy for the approach of two hydrogen atoms to a hydrogen molecule. We can make no definite statement about this, since we have not calculated the necessary surface. We thus come to the conclusion that H_2 is at best $\frac{1}{6}$ as efficient as H. This is in agreement with the results of Amdur rather than those of Steiner. Only if the transfer of energy between the rotation of the colliding H_2 molecule and the associating atoms is much greater than our present knowledge of the potential surface indicates could the calculated order of efficiencies be reversed.

The reasoning of the preceding paragraph indicates why hydrogen molecules are so much more efficient than others for the transfer of energy. Other authors have assumed that it is because the mechanism is one of transfer of rotational energy to vibrational and that since hydrogen has such a small moment of inertia it can transfer a large amount of energy in a single quantum. From the preceding considerations it would seem that the efficiency of hydrogen may be due rather to the fact that it can so readily form a complex with the reacting substances, since its moment of inertia is so small that it is in a favorable configuration about half of the time at room temperature.

We see that in general, according to the point of view which has here been put forth, the ability to transfer energy is intimately connected with reactivity. This is in agreement with most of the available data. Franck and Eucken[13] have reached the same conclusions through more qualitative methods. Our calculation for the 3 H case shows how any other case may be treated quantitatively. The method is valid not only for actual chemical reactions but also in cases in which no bonds are formed or broken. Thus it can be applied to the data obtained in sound dispersion experiments, where all the data indicate that energy is most easily transferred among molecules that can react with each other.[14] The method may also be applied to the study of the maintenance of the high pressure rate of unimolecular reactions by foreign gases. Here too most of the observed facts are fitted by the theory. As we might expect, comparatively inert substances vary considerably in the efficiency with which they maintain the rate. This is shown by the work of Volmer and his collaborators on N_2O.[15] Returning to the recombination of hydrogen atoms, Bonhoeffer[16] has made a qualitative determination of the relative effi-

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[13] Franck and Eucken, Zeits. f. physik. Chemie **B20**, 460 (1933).

[14] Eucken and Becher, Zeits. f. physik. Chemie **B20**, 467 (1933); Kneser and Knudsen, Ann. d. Physik **21**, 682 (1935); Richards and Reid, J. Chem. Phys. **2**, 206 (1934).

[15] Volmer and Froehlich, Zeits. f. physik. Chemie **B19**, 89 (1932).

[16] Bonhoeffer, Zeits. f. physik. Chemie **119**, 385, 475 (1926).

ciency of various gases as third bodies. The order he finds agrees very well with the relative reactivities. The data of Senftleben and Hein,[17] however, are in definite disagreement with our theory, but the absolute rate for the recombination of hydrogen atoms found by these authors is very much lower than that of Amdur or Steiner.

The method of potential energy surfaces thus provides us with a clear picture of homogeneous catalytic processes. It forms a convenient basis for a satisfactory discussion of the problems of energy transfer.

[17] Senftleben and Hein, Ann. d. Physik **22**, 1 (1935).

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

A Summary of Experimental Activation Energies of Elementary Reactions Between Hydrogen and the Halogens

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(Received July 22, 1935)

Existing experimental data on reactions between hydrogen and the halogens have been analyzed to give values of the activation energies of the intermediate reactions involved. These are compared with calculated values due to Eyring and Wheeler.

EVIDENCE has been accumulating over a period of years that reactions between molecules and free atoms may have appreciable activation energies. This evidence is in the main not direct, but must be deduced from considerations as to the most probable mechanism of reaction. In this paper the experimental evidence for reactions of hydrogen and the halogens is reviewed and tentative values of the activation energies are suggested. The reactions in question are of the types:

$$H+X_2\rightarrow HX+X, \qquad X+H_2\rightarrow HX+H,$$
$$H+HX\rightarrow X+H_2.$$

Hydrogen-Bromine Reactions

This reaction system has been quite thoroughly covered in both its theoretical and experimental aspects by Kassel in his *Kinetics of Homogeneous Gas Reactions*. However, newer numerical data have made possible more exact conclusions as to the individual reactions. The chain consists of the steps:

$$Br_2 \xrightarrow{k_1} 2Br, \tag{1}$$

$$Br+H_2 \xrightarrow{k_2} HBr+H, \tag{2}$$

$$H+Br_2 \xrightarrow{k_3} HBr+Br, \tag{3}$$

$$H+HBr \xrightarrow{k_4} H_2+Br, \tag{4}$$

$$Br+Br \xrightarrow{k_5} Br_2, \tag{5}$$

which lead to the theoretical expression:

$$\frac{d[HBr]}{dT}=2k_2(k_1/k_5)^{\frac{1}{2}}\frac{[H_2][Br_2]^{\frac{1}{2}}}{1+k_4/k_3[HBr]/[Br_2]}.$$

From experimental researches by Bodenstein and Lind,[1] confirmed by Bach, Bonhoeffer and Moelwyn-Hughes[2] $2k_2(k_1/k_5)^{\frac{1}{2}}$ and k_4/k_3 have been determined. Since $k_5/k_1=K_D$, the dissociation constant of bromine, which is now well known, k_2 may be evaluated from the knowledge of $2k_2(k_1/k_5)^{\frac{1}{2}}$. The temperature coefficient of k_2 will give A_2, the activation energy of reaction (2). If the data of Gordon and Barnes[3] on K_D are used, both sets of results yield $A_2(Br+H_2)=17.7$ Kg.Cals.

[1] Bodenstein and Lind, Zeits. f. physik. Chemie **57**, 168 (1907).
[2] Bach, Bonhoeffer and Moelwyn-Hughes, Zeits. f. physik. Chemie **B27**, 71 (1934).
[3] Gordon and Barnes, J. Chem. Phys. **1**, 792 (1933).

From this value of A_2 theoretical reaction rates may be calculated and are found to agree quite well with observed values when reasonable molecular diameters (3×10^{-8} cm) are used.

Reaction (4), $H+HBr\rightarrow H_2+Br$, is the reverse of the reaction just studied. The difference in activation energies between process (2) and the one just given may then be taken as the heat of reaction. This may be calculated thermochemically from the data of Gordon and Barnes,[3] who give these values:

$$Br_2\rightarrow 2Br, \qquad \Delta E_0=45.23 \text{ Kg.Cals.}$$
$$HBr\rightarrow \tfrac{1}{2}H_2+\tfrac{1}{2}Br_2, \qquad \Delta E_0=11.99 \text{ Kg.Cals.}$$

and from the recent work of Beutler,[4] who finds for hydrogen

$$H_2\rightarrow 2H, \qquad \Delta E_0=102.68 \text{ Kg.Cals.}$$

Proper combination of these leads to the result

$$H+HBr\rightarrow H_2+Br, \qquad \Delta E_0=-16.7 \text{ Kg.Cals.}^{4a}$$

By direct subtraction a value, $A_4(H+HBr)=1.0$ Kg.Cals., is obtained for reaction (4). This value of 1 kilogram calorie is in accord with the results of Cremer, Curry, and Polanyi,[5] who attempted to determine the rate of this reaction by passing atomic hydrogen into HBr. The reaction was too rapid for their measurements, which were made by means of the para to ortho-hydrogen conversion, so that they could only conclude that A_4 was less than 3.0 Kg.Cals.

The ratio k_4/k_3 was accurately determined by Bodenstein and Jung,[6] who found a value of 1/8.4 practically independent of temperature from 0° to 300°C, indicating that the A/RT terms are the same for reactions (3) and (4), for otherwise the ratio k_4/k_3 would vary with temperature. The constant factor of 1/8.4 may be ascribed to an "orientation factor," but whatever the explanation, it has no bearing on present reasoning. It follows for reaction (3) that $A_3(H+Br_2)=1.0$ Kg.Cals.

[4] Beutler, Zeits. f. physik. Chemie **B27**, 287–302 (1934).
[4a] Kassel gives −14.5 Kg.Cals. for the heat of this reaction. This seems to be an error.
[5] Cremer, Curry and Polanyi, Zeits. f. physik. Chemie **B23**, 445 (1933).
[6] Bodenstein and Jung, Zeits. f. physik. Chemie **121**, 127 (1926).

Hydrogen-Chlorine Reactions

The attempt to evaluate some of the constants in the hydrogen-chlorine reaction is a more difficult task, since the reaction mechanism has not been as definitely settled as in the hydrogen-bromine reaction. The Nernst chain mechanism is well established, however.[7] According to this scheme the probable reactions in the photochemical hydrogen-chlorine combination are

$$Cl_2+h\nu\xrightarrow{k_1}2Cl, \tag{1}$$
$$Cl+H_2\xrightarrow{k_2}HCl+H, \tag{2}$$
$$H+Cl_2\xrightarrow{k_3}HCl+Cl, \tag{3}$$
$$H+HCl\xrightarrow{k_4}H_2+Cl. \tag{4}$$

The chain-ending mechanisms may possibly be any of the following

$$Cl+Cl+M\xrightarrow{k_5}Cl_2+M \tag{5}$$
$$Cl+X\xrightarrow{k_6}ClX, \tag{6}$$
$$H+X\xrightarrow{k_7}HX, \tag{7}$$
$$H+H+M\xrightarrow{k_8}H_2+M \tag{8}$$
$$H+O_2+M\xrightarrow{k_9}HO_2+M \tag{9}$$
$$H+O_2\xrightarrow{k_{10}}HO_2 \tag{10}$$
$$Cl+O_2\xrightarrow{k_{11}}ClO_2. \tag{11}$$

In this scheme X represents any foreign chain-breaker other than oxygen, such as the wall, or, with Bodenstein,[8] a volatile compound of silicon. M is a third body, either H_2, Cl_2 or HCl.

The most significant experiment toward the evaluation of activation energies in this series of

[7] For a complete discussion see Semenov, *Chemical Kinetics and Chain Reactions*, pp. 98–115.
[8] Bodenstein and Unger, Zeits. f. physik. Chemie **B11**, 253 (1931).

reactions was a direct determination by Rodebush and Klingelhoeffer[9] of the rate of reaction (2). By passing atomic chlorine into hydrogen they determined the probability of a chlorine atom's reacting, using the formula

$$W=\frac{\text{HCl formed}}{\text{Cl introduced}}/2Z',$$

where Z' is the number of collisions between Cl and H_2 calculated from kinetic theory, and W is the probability of reaction at each collision. Rodebush and Klingelhoeffer have calculated A_2 from the temperature coefficient of W. We have also calculated A_2 directly from the formula

$$W=e^{-A_2/RT}.$$

The results by these two methods accord very well and give for $A_2(Cl+H_2)$ a value of 6 Kg.Cals.

The problem may also be indirectly approached through a consideration of the photochemical reaction in the absence of oxygen. Bodenstein and Unger,[8] using the following set of reactions taken from the larger number presented before:

$$Cl_2+h\nu \xrightarrow{k_1} 2Cl, \quad (1)$$

$$Cl+H_2 \xrightarrow{k_2} HCl+H, \quad (2)$$

$$H+Cl_2 \xrightarrow{k_3} HCl+Cl, \quad (3)$$

$$H+HCl \xrightarrow{k_4} H_2+Cl, \quad (4)$$

$$Cl+X \xrightarrow{k_6} ClX, \quad (6)$$

$$H+X \xrightarrow{k_7} HX, \quad (7)$$

developed this theoretical expression:

$$\frac{d[HCl]}{dt}=\frac{4k_2k_3\cdot I_{abs.}[H_2]\cdot[Cl_2]}{k_2k_7[H_2]+k_3k_6[Cl_2]+k_4k_6[HCl]}.$$

On the other hand they found experimentally,

$$d[HCl]/dt=kI_{abs.}[H_2].$$

This empirical equation has recently been checked by Potts and Rollefson.[10] It could only be accounted for if reactions (4) and (7) were very slow compared to (3) and (6), respectively. When only reactions (1), (2), (3) and (6) are considered, the theoretical expression found is

$$d[HCl]/dt=(2k_2/k_6)[H_2]/[X]I_{abs.},$$

which agrees with the theoretical equation if [X] be constant. If we assume that all of the terms in this expression are practically independent of temperature except k_2/k_6, the temperature coefficient will depend on k_2/k_6 and gives the difference in activation energy between reactions (2) and (6).

Hertel[11] found the temperature coefficient in the absence of oxygen to be 1.37 between 25 and 35°. This calculates to a difference in activation energies of 5.9 Kg.Cals. Potts and Rollefson[10] by the same method find the difference to be 5.8 Kg.Cals. These values agree well with the absolute value found by Rodebush and Klingelhoeffer for reaction (2) alone, indicating that (Cl+X) requires no activation. In any case this result is a minimum activation energy for reaction (2). We, therefore, write

$$A_2(Cl+H_2)=6.0 \text{ Kg.Cals.}$$

The activation for the reverse reaction may be obtained from a coupling of the above result with thermal data. Best present day values as compiled by B. Lewis and von Elbe[12] give

$$HCl \rightleftarrows \tfrac{1}{2}H_2+\tfrac{1}{2}Cl_2, \qquad \Delta E_0=+21.98 \text{ Kg.Cals.}$$
$$Cl_2 \rightleftarrows 2Cl, \qquad \Delta E_0=+56.9 \text{ Kg.Cals.}$$

A proper combination of these with the value given before for hydrogen dissociation yields

$$Cl+H_2 \rightarrow HCl+H, \qquad \Delta E_0=1.0 \text{ Kg.Cals.}$$

By subtracting this from $A_2(Cl+H_2)$ one obtains the activation energy of the reverse reaction, $A_4(H+HCl)=5$ Kg.Cals.

The evaluation of the energy of activation for reaction (3) is less certain. The reaction occurs

[9] Rodebush and Klingelhoeffer, J. Am. Chem. Soc. **55**, 130 (1933).

[10] Potts and Rollefson, J. Am. Chem. Soc. **57**, 1027 (1935).

[11] Hertel, Zeits. f. physik. Chemie **B15**, 325 (1931).

[12] B. Lewis and von Elbe, J. Am. Chem. Soc. **57**, 612 (1935).

rapidly at room temperatures[13, 14] but the measurements are not of such a type that activation energies may be calculated from them. The matter must be attacked indirectly through a consideration of experiments on the photochemical combination in the presence of oxygen, along with some other data.

In the presence of oxygen reactions (1), (2) and (3) start and continue the chain. Reaction (4) may be omitted since it was shown that it is negligible compared to (3). The chain-ending mechanism is believed to be

$$H+O_2+M \xrightarrow{k_9} HO_2+M, \qquad (9)$$

where M is a third body. The reasons for this belief will be brought out later. These reactions lead to the following kinetic equation:

$$\frac{d[HCl]}{dt}=k_1[Cl_2]+\frac{2k_1k_3}{k_9}\frac{[Cl_2]^2}{[M][O_2]}. \qquad (a)$$

Since with moderate oxygen content the chain length is still of the order of 100 and $k_1[Cl_2]$ involves only the first step, the equation may be approximated to

$$\frac{d[HCl]}{dt}=\frac{2k_1k_3}{k_9}\frac{[Cl_2]^2}{[M][O_2]}. \qquad (b)$$

The temperature coefficient of the rate in this case depends chiefly on k_3/k_9. Values of the temperature coefficient per 10°, found by various authors at room temperature are: 1.12 by Hertel,[11] 1.19 by Padoa,[15] 1.10 by Porter, Bardwell and Lind.[16] The activation energy calculated from these values will represent (A_3-A_9). Evaluation gives for (A_3-A_9) 2.1, 2.9 and 1.8 Kg.Cals., respectively.

Krauskopf and Rollefson[17] found (A_3-A_9) in a different way. The partition of the hydrogen reacting in a system containing oxygen and chlorine between H_2O and HCl was directly determined. Applications of equation (a) above and the equation

$$d[H_2O]/dt=k_1[Cl_2],$$

assuming one molecule of water formed for each hydrogen atom reacting with oxygen leads to

$$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2 \text{ reacting}}=U$$

$$=\frac{2}{3+2k_3/k_9\cdot[Cl_2]/[O_2][M]}.$$

From the observation that when $[O_2]/[Cl_2]$ is 20, $U=0.57$ at 0° and 0.40 at 85°C, they calculate the difference (A_3-A_9) to be 1.6 Kg.Cals.

All these values represent a minimum for the activation energy A_3, since A_9 is not likely to be negative. This gives $A_3(H+Cl_2)$ is greater than 2 Kg.Cals.

The upper limit may also be determined. Bodenstein and Unger[8] concluded from their data that HCl did not inhibit the reaction in the absence of oxygen, and that consequently reaction (4) was slow compared to reaction (3). This is confirmed by the work of Potts and Rollefson.[10] Let us therefore make the assumption that

$$k_3/k_4>100.$$

Since we wish to make sure of having a maximum value for A_3, an "orientation factor" of 1/10 will be allowed for H+HCl as was indicated for H+HBr. Then

$$k_3/k_4=(Z_{13}e^{-A_3/RT}/0.1Z_{12}e^{-A_4/RT})>100.$$

From this is obtained $A_4-A_3>1.4$ Kg.Cals. Since A_4 has already been determined to be 5 Kg.Cals., this gives $A_3<3.6$ Kg.Cals.

Another method for obtaining a maximum value follows. Bonhoeffer and a co-worker[18] tried to measure the para- to ortho-hydrogen conversion in a mixture of para-hydrogen and chlorine when illuminated. Their method was accurate enough to determine one percent of para- to ortho-conversion, but they were unable to detect any change. This means that

[13] Boehm and Bonhoeffer, Zeits. f. physik. Chemie **119**, 385 (1926).
[14] Marshall, J. Phys. Chem. **29**, 842 (1925).
[15] Padoa and Buttironi, Atti. Linc. **25**, 215 (1916); Gazz. **47**, 6 (1917).
[16] Porter, Bardwell and Lind, J. Am. Chem. Soc. **48**, 2603 (1926).
[17] Krauskopf and Rollefson, J. Am. Chem. Soc. **56**, 325 (1934).
[18] Geib and Hartek, Zeits. f. physik. Chemie **B15**, 116 (1932).

$$H+H_{2_{para}} \overset{k_{p0}}{\rightarrow} H_{2_{ortho}}+H$$

is slow compared with

$$H+Cl_2 \overset{k_3}{\rightarrow} HCl+Cl.$$

The assumption may be made then that

$$k_{p0}/k_3 < 0.01.$$

Then we have

$$k_{p0}/k_3 = (Z_{12}^{-A_{p0}/RT}/Z_{12}^{-A_3/RT}) < 0.01.$$

Taking the Z_{12} factors in this case to be the same, we have

$$e^{-A_{p0}/RT}/e^{-A_3/RT} < 0.01$$

or $A_{p0}-A_2 < 2.8$ Kg.Cals. Since A_{p0} has been determined to be in the neighborhood of 7.0 Kg.Cals.[19] a maximum value for A_3 of 4.2 Kg.Cals. is obtained.

Since a minimum value for A_3 of 1.6 to 2.9 Kg.Cals. has been obtained and a maximum value of 3.6 to 4.2 Kg.Cals., a value, $A_3(H+Cl_2) = 2$–3 Kg.Cals., is indicated.

It is now necessary to return to a consideration of the chain-ending mechanism in the presence of oxygen, for which

$$H+M+O_2 \rightarrow HO_2+M \qquad (9)$$

has been used. Various experiments have quite definitely established that the chain-ending mechanism must involve a reaction of hydrogen atoms with oxygen rather than chlorine atoms with oxygen. Thus, Schwab and Friess[20] passed atomic chlorine into oxygen and found no measurable reaction whatever. Further, the logical product of a reaction of chlorine atoms with oxygen, ClO_2, is known to be a very strong inhibitor for the reaction,[21] so that if this product were formed, the rate would decrease rapidly. No such result has ever been observed. Thirdly, a study of yields of H_2O and HCl in very high oxygen-containing mixtures led Krauskopf and Rollefson[17] to the conclusion that $(Cl+O_2)$ could play only a very small part, if any, in stopping the chains. Lastly the types of kinetic expressions obtained experimentally indicate that oxygen breaks the chains by reaction with hydrogen atoms.

Bodenstein and Schenck[22] first showed that the reaction of hydrogen atoms with oxygen was logically a three-body process. They observed that although the activation energy of the atomic H and O_2 reaction was 2 Kg.Cals. less than that of H and Cl_2 and consequently should proceed 50 times as fast as the latter, nevertheless comparative yields of HCl and H_2O in $H_2-O_2-Cl_2$ mixtures containing equal amounts of Cl_2 and O_2 showed the rate of $H+Cl_2$ to be twenty times faster than $H+O_2$. This meant that only 1 in 1000 (20 times 50) of the bimolecular collisions with sufficient activation energy between hydrogen and oxygen was effective. Since 1 : 1000 is approximately the ratio of trimolecular to bimolecular collisions, it appeared that $H+O_2$ must involve a third body.

This position has received confirmation from Bates[23] who shows quite conclusively that the chain-ending reaction is a three-body process. Cook and Bates[23] studied the inhibition of the photodecomposition of HI in presence of oxygen, which involves $(H+O_2)$. Considering the reactions

$$H+HI \overset{k_\alpha}{\rightarrow} H_2+I, \qquad (\alpha)$$

$$H+O_2 \overset{k_\beta}{\rightarrow} HO_2 \qquad (\beta)$$

they found that using a bimolecular reaction for (β), k_α/k_β was about 10 at 100 mm HI and 100 mm O_2, but decreased to 3 when 300–400 mm of N_2 was added. If a trimolecular reaction were employed,

$$H+M+O_2 \overset{k_\beta'}{\rightarrow} HO_2+M \qquad (\beta')$$

then the ratio k_α/k_β' remained constant throughout. Thus the chain-ending mechanism seems quite definitely to be a three-body process.

The theory on which the values in this reaction chain are based is that developed by Bodenstein and various co-workers. Some recent

[19] Geib and Hartek, Zeits. f. physik. Chemie, Bodenstein-band 849 (1931).
[20] Schwab and Friess, Zeits. f. Electrochim. **39**, 586 (1933).
[21] Chapman and MacMahon, J. Chem. Soc. **97**, 845 (1909).
[22] Bodenstein and Schenck, Zeits. f. physik. Chemie **B20**, 420 (1933).
[23] Bates and Lavin, J. Am. Chem. Soc. **55**, 81 (1933); Cook and Bates, J. Am. Chem. Soc. **57**, 1775 (1935).

researches, notably the extensive ones of Norrish and Ritchie,[24] are at variance with this scheme. Thus, while Bodenstein had found a variation of the rate of reaction in oxygen-free mixtures depending on the first power of the light absorbed, Norrish and Ritchie found a dependence on the 0.6 power. This is explained on the basis that the chain-ending mechanism is a recombination of chlorine atoms, rather than a reaction of the type

$$Cl+X\rightarrow ClX.$$

Thus, either chain-breaking mechanism may be correct, depending on the experimental conditions. This is confirmed by Potts and Rollefson,[10] who found a first power dependence at room temperature and a 0.5 power dependence at liquid-air temperatures. Since $Cl+H_2$ occurs 1 in 10^5 collisions at room temperature and only 1 in 10^8 at liquid-air temperatures, [Cl] will be enormously increased and thus

$$Cl+Cl+M\rightarrow Cl_2+M$$

the rate of which depends on the square of the chlorine concentration, will be greatly favored at liquid-air temperatures as compared to

$$Cl+X\rightarrow ClX$$

the rate of which depends only on the first power of the chlorine concentration. However, either chain-breaking mechanism leads to the same type of variation with temperature and allows the same conclusions to be drawn concerning the activation energy of $(Cl+H_2)$. The Bodenstein mechanism has been used because Hertel,[11] and Potts and Rollefson,[10] whose values for the temperature coefficient were used, both found a first-power dependence on light absorbed.

A second difference is more serious. Bodenstein and Unger[8] found no inhibition by HCl in the absence of oxygen, and Bodenstein and Schenck[22] found none in the presence of oxygen. Norrish and Ritchie[24] find serious retardation by that substance in both cases. They ascribe this to the reaction $H+HCl\rightarrow H_2+Cl$ which they consider to be comparable in rate to $H+Cl_2\rightarrow HCl+Cl$. This is not only opposed to Bodenstein's mechanism, but also is inconsistent with their own results. For, from thermodynamic considerations $(Cl+H_2)$ and $(H+HCl)$ must have approximately similar rates[10] ($\Delta E_0=1.0$ cals.). On Norrish and Ritchie's assumptions, therefore

$$Cl+H_2\xrightarrow{k_2}HCl+H \quad \text{and} \quad H+Cl_2\xrightarrow{k_3}HCl+Cl$$

have rate constants of the same order of magnitude. Thus, in an equimolecular reaction system, since these two reactions must be proceeding at the same rate in order to maintain steady state atomic concentrations

$$k_2[Cl][H_2]\cong k_3[H][Cl_2],$$

whence

$$[Cl]\cong[H].$$

If this be true, then $Cl+Cl+M\rightarrow Cl_2+M$, $H+Cl+M\rightarrow HCl+M$, and $H+H+M\rightarrow H_2+M$ should all be effective in breaking chains. Yet neither of the latter two reactions enter into Norrish and Ritchie's kinetic expression and they state that a mechanism which considers these as chain-breaking reactions does not fit the experimental facts. Either both

$$H+HCl\rightarrow H_2+Cl$$

and

$$\left.\begin{matrix}H+H+M\rightarrow H_2+M\\ H+Cl+M\rightarrow HCl+M\end{matrix}\right\}$$

must enter the kinetic expression or neither can enter. The evidence indicates the latter.

So, although Norrish and Ritchie have undoubtedly obtained excellent experimental results, their explanation of them does not hold. On the other hand, their results in the presence of oxygen are easily explained by adopting the three-body process $(H+M+O_2)$ as the chain-breaking mechanism, where HCl is an effective third body. Their results in the absence of oxygen are only partly explained by the trimolecular recombination of chlorine atoms. However, some light has recently been thrown on this point by the experiments of Rodebush and Spealman,[25] which seem to indicate that H+HCl may occur rapidly as a catalytic reaction on the surface of Pyrex. If the walls of Norrish and Ritchie's vessels were active in this way, their results are easily accounted for. In view of these facts the

[24] Norrish and Ritchie, Proc. Roy. Soc. **A140**, 112, 713 (1933).

[25] Rodebush and Spealman, J. Am. Chem. Soc. **57**, 1040 (1935).

Bodenstein mechanism seems to be the correct one to use to obtain the rates of the homogeneous reactions.

Hydrogen-Iodine Reaction

Work on the atomic reactions in this case is quite scanty since the ordinary combination is a molecular process. However, there is sufficient evidence to obtain approximate values.

From his studies of the photodecomposition of hydrogen iodide in presence of oxygen, Bates[23] concludes that for the reactions

$$H+HI \xrightarrow{k_1} H_2+I, \qquad (1)$$

$$H+O_2+M \xrightarrow{k_9} HO_2+M, \qquad (9)$$

k_1 is about ten times k_9 when k_9 is regarded as a bimolecular constant. Later work indicated that reaction (9) is in fact trimolecular, as it is written above. Since the ratio of bimolecular to trimolecular collisions is of the order of 1000, k_1 would be 1000 times k_9 if every collision were effective in both reactions. Allowing an orientation factor of 10 for reaction (1), as was found for the analogous reaction $H+HBr \rightarrow H_2+Br$, this is reduced to a factor of 100, which is to be compared to the observed ratio of 10. One concludes that reaction (1) may require an activation energy, $A_1(H+HI) \sim 1$ Kg.Cal.

The value for the reverse of this reaction may be found from thermal data. Beutler's[4] value for hydrogen was

$$H_2 \rightleftarrows 2H, \qquad \Delta E_0 = 102.68 \text{ Kg.Cals.}$$

Landolt-Börnstein[26] give

$$H_2+I_2 \rightleftarrows 2HI, \qquad \Delta E_0 = -2.8 \text{ Kg.Cals.}$$

The value for the dissociation of iodine is taken from Brown[27]

$$I_2 \rightleftarrows 2I, \qquad \Delta E_0 = 35.4 \text{ Kg.Cals.}$$

These lead to a value

$$H+HI \rightleftarrows H_2+I, \qquad \Delta E_0 = -32.3 \text{ Kg.Cals.}$$

The activation energy of the reverse reaction is obtained by addition and gives $A_3(I+H_2) = 33$ Kg.Cals.

From the observation of Farkas and Bonhoeffer[28] that 15 percent of iodine completely inhibits the photodecomposition of HI they conclude that

$$H+I_2 \xrightarrow{k_2} HI+I \qquad (2)$$

occurs 100 times as frequently as reaction (1) or therefore at practically every collision. This means that $A_4(H+I_2) \sim 0$.

Comparison of Values

A comparison of the results obtained by this study with those obtained by theoretical calculation[29] by Eyring's method by using a 14 percent Coulombic term is shown in Table I. The results agree quite well as to order, but the calculated values tend to run higher. It may be noted that a larger Coulombic term would lead to better agreement in the majority of cases.

Table I.

	$H+Cl_2$	$H+Br_2$	$H+I_2$	$H+HCl$	$H+HBr$	$H+HI$	$Cl+H_2$	$Br+H_2$	$I+H_2$
Experimental	3	1.0	0	5	1	1	6.0	17.7	33
Eyring	2.4	2.2	1.4	11.8	6.6	7.5	12.8	24.0	40

[26] Landolt-Börnstein, *Tabellen*, Erster Erganzungsband, p. 809.

[27] Brown, Phys. Rev. **38**, 709 (1931).

[28] Farkas and Bonhoeffer, Zeits. f. physik. Chemie **132**, 235 (1928).

[29] Private communication, H. Eyring and A Wheeler.

The Group Relation Between the Mulliken and Slater-Pauling Theories of Valence

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(Received October 7, 1935)

By means of the group theory of characters, it is shown that there is an intimate relation between Mulliken's molecular orbitals and the Slater-Pauling directed wave functions. One can pass from the former to the latter by making a simple transformation from an irreducible to a reducible representation. Consequently the same formal valence rules are usually given by either method, and one can understand generally why wave functions of the central atom which are nonbonding in Mulliken's procedure are likewise never employed in constructing Pauling's "hybridized" linear combinations.

TWO distinct viewpoints have been particularly developed in applying quantum mechanics to problems of valence,[1] namely, the Heitler-London-Pauling-Slater method of the electron pair bond, and the method of molecular orbitals used by Hund, Lennard-Jones, Mulliken, and others. The two procedures represent different approximations to the solution of a complicated secular equation. The method of molecular orbitals permits factorization into one-electron problems, but at the expense of adequate cognizance of the terms due to electron repulsion, which are too fully recognized in the H-L-P-S procedure. A characteristic feature of the latter is the "hybridization," whereby linear combinations of states of different azimuthal quantum number for the central atom are necessary in fields of, for example, tetrahedral symmetry. It was shown by the writer that in the case of carbon compounds the two theories, though superficially different, predicted similar results on geometrical arrangement.[2] It is the purpose of the present paper to show that the equivalence is general in the sense that one formulation will give the same formal stereochemical valence principles as the other. Thus it is futile to discuss whether the Mulliken or Pauling theory will give better working rules in compounds formally amenable to electron pair treatment. Both, for instance, suggest the now classic Pauling square configuration for $Ni(CN)_4^{--}$ in view of the diamagnetism of this ion. (A tetrahedral model would give paramagnetism with either method.[3]) One can only inquire which procedure involves the more reasonable hypotheses. It seems to us that in the case of the transition elements, one must probably decide in favor of the Mulliken formation as a simple qualitative description, though perhaps a poor quantitative approximation. It is difficult to believe, for instance, that the $Fe(CN)_6^{4-}$ radical has the Pauling structure $Fe^{4-}(CN)_6$, since the Fe ion certainly is unwilling to swallow four extra electrons. The conventional ionic model $Fe^{++}(CN^-)_6$, on the other hand, probably goes too far in the other direction. The Mulliken viewpoint has here the advantage of allowing an arbitrary distribution of charge between Fe and $(CN)_6$, depending on how one weights the various atomic orbitals in forming a molecular orbital as a linear combination of them. Only a limited significance should, however, be given to any purported preference between the two methods, as each represents a solution of the secular equation only under certain extreme conditions. The true wave function is in reality a combination of H-LJ-M and H-L-P-S functions, along with many ingredients intermediate between these two extremes, and so either theory is bound to have some semblance of truth. The latter functions, for instance, can be amplified

[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); J. C. Slater, Phys. Rev. **38**, 1109 (1931); R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751; **43**, 279 (1932–3); J. Chem. Phys. **1**, 492 (1933); **3**, 375, 506 (1935). For other references, or more detailed introduction on the methods which we compare, see J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935). Other workers besides Mulliken have contributed to the molecular orbital procedure, but we sometimes refer to the latter as Mulliken's method, since we are concerned with the application to polyatomic molecules in the light of symmetry groups, an aspect considered primarily by Mulliken.

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[3] Cf. Pauling, reference 1, and J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 206, 221 (1935).

by taking linear combinations with terms representing different stages of charge transfer until finally just the right polarity is obtained.

Molecular Orbitals

We shall confine our discussion to the case where a central atom attaches n atoms arranged in some symmetrical fashion (tetrahedron, square, etc.) characteristic of a crystallographic point group.[4] Let $\psi(\Gamma)$ be a wave function of the central atom which has the proper symmetry, i.e., whose transformation scheme under the covering operations of the group is that characteristic of some irreducible representation Γ. Let ψ_i be a wave function of attached atom i. We shall assume that only one orbital state need be considered for each attached atom, and that this state is either an s state or else is symmetric (as in a $2p\sigma$ bond) about the line joining the attached to the central atom. The method of molecular orbitals in its simplest form[5] seeks to construct solutions of the form

$$\psi=\psi(\Gamma)+\Sigma_i a_i\psi_i. \tag{1}$$

The coefficients a_i must be so chosen that $\Sigma_i a_i\psi_i$ transforms in the fashion appropriate to the irreducible representation Γ. Now the important point is that bases for only certain irreducible representations can be constructed out of linear combinations of the ψ_i. To determine which, one ascertains the group characters associated with the transformation scheme, usually reducible, of the original attached wave functions ψ_i before linear combinations are taken. This step is easy, as the character χ_D for a covering operation D is simply equal to q, where q is the number of atoms left invariant by D. This result is true inasmuch as D leaves q of the atoms alone, and completely rearranges the others, so that the diagonal sum involved in the character will contain unity q times, and will have zeros for the other entries. The scheme for evaluating the characters is reminiscent of that in the group theory of molecular vibrations employed by Wigner and by E. B. Wilson, Jr.,[6] but is simpler since we are not interested in displacements of atoms from equilibrium, and in consequence all nonvanishing entries are unity rather than some root of unity. After the characters have been found, the determination of the constituent irreducible representations proceeds in the usual way by means of the theorem that the unresolved characters must equal the sum of the primitive characters contained therein.

As an illustration, we may consider a complex containing six atoms octahedrally arranged, i.e., located at the centers of the six cube faces. Then the symmetry group is the cubic one O_h, and the characters associated with the arrangement of attached atoms are

$$\begin{array}{cccccccccc} & E & C_2 & C_4 & C_2' & C_3 & I & IC_2 & IC_4 & IC_2' & IC_3 \\ \chi= & 6 & 2 & 2 & 0 & 0 & 0 & 4 & 0 & 2 & 0. \end{array} \tag{2}$$

Here $\chi(C_4)$, for instance, means the character for the covering operation consisting of rotation about one of the fourfold or principal cubic axes (normals to cube faces) by $2\pi/4$. Any rotation about such an axis leaves two atoms invariant, and hence $\chi(C_2)=\chi(C_4)=2$. On the other hand, $\chi(C_2')=\chi(C_3)=0$ since no atoms are left invariant under rotations about the twofold or secondary cubic axes (surface diagonals) or about the threefold axes (body diagonals). Inversion in the center of symmetry is denoted by I. By using tables of characters for the group O_h, one finds that the irreducible representations contained in the character scheme (2) are, in Mulliken's notation,[4]

$$A_{1g},\ E_g,\ T_{1u}. \tag{3}$$

The irreducible representations corresponding to various kinds of central orbitals are shown below:

$$\begin{array}{lccccc} \text{orbit} & s & p & d\gamma & d\epsilon & \overbrace{\qquad f \qquad} \\ \text{rep.} & A_{1g} & T_{1u} & E_g & T_{2u} & A_{2u},\ T_{1u},\ T_{2u}. \end{array} \tag{4}$$

The notation for the various kinds of d wave functions is that of Bethe,[7] *viz.*,

[4] See R. S. Mulliken, Phys. Rev. **43**, 279 (1933) or references 6 and 7 if further background is desired on the aspects of group theory and crystallographic symmetry which we use.

[5] Called by Mulliken the LCAO ("linear combination of atomic orbitals") form. For a critique of this type of approximation see R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935). It appears to have been first suggested by Lennard-Jones.

[6] E. Wigner, Gött. Nachr., p. 133 (1930); E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934); Phys. Rev. **45**, 706 (1934).

[7] H. Bethe, Ann. d. Phvsik **3**, 165 (1929).

TABLE I.

SYMMETRY	CENTRAL ORBITALS s	p	d	f	ATTACHED ORBITALS No.	REPRESENTATIONS
Tetrahedral (T_d)	A_1	T_2	$E(d\gamma)$, $T_2(d\epsilon)$	A_1, T_1, T_2	4	A_1, T_2
Trigonal (D_{3h})	A_1'	A_2'', E'	A_1', E', E''	A_1', A_2', A_2'', E', E''	3	A_1', E'
					6	A_1', A_2'', E', E''
Tetragonal (D_{4h})	A_{1g}	A_{2u}, E_u	A_{1g}, B_{1g}, B_{2g}, E_g	A_{2u}, B_{1u}, B_{2u}, $2E_u$	4	A_{1g}, B_{1g}, E_u
					8	A_{1g}, A_{2u}, B_{1g}, B_{2u}, E_u, E_g

$$\psi(d\gamma_1)=(1/12)^{\frac{1}{2}}f(r)(3z^2-r^2),\quad \psi(d\gamma_2)=\tfrac{1}{2}f(r)(x^2-y^2), \tag{5}$$

$$\psi(d\epsilon_1)=f(r)xy,\quad \psi(d\epsilon_2)=f(r)xz,\quad \psi(d\epsilon_3)=f(r)yz. \tag{6}$$

By comparison of (3) and (4) we see that is it impossible for $d\epsilon$ orbitals to form any partnerships with attached orbitals, in agreement with Mulliken's conclusion[8] that $d\gamma$ rather than $d\epsilon$ is particularly adapted to forming octahedral bonds. Mulliken's arguments were mainly of a qualitative nature. The preceding considerations enable us to formulate the situation more succinctly, as they show that the $d\epsilon$ orbitals are entirely nonbonding.

In Table I we give the irreducible representations, in Mulliken's notation, contained in the central and attached orbitals for compounds of other types of symmetry. When 3 or 4 atoms are trigonally or tetragonally attached, we have supposed that the plane of these atoms is a plane of symmetry, as in $(NO_3)^-$ or $Ni(CN)_4^{--}$. When there is no such symmetry plane, as in NH_3, the distinctions between u and g, or between primes and double primes, are to be abolished,[9] and the symmetries degenerate to C_{3v}, C_{4v} instead of D_{3h}, D_{4h}. When 6 atoms are attached in the scheme D_{3h}, or 8 in D_{4h}, they are arranged respectively at the corners of a trigonal and a square prism.

The results given in Table I are obtained by the same method as in the octahedral example. The explicit forms of the linear combinations of the attached orbitals which transform irreducibly, or in other words the values of the coefficients a_i in (1) have been tabulated by Van Vleck and Sherman[10] in many instances, and so need not be repeated here. The a_i for the octahedral case are also given in Eqs. (2)–(7) of the following paper.

Note particularly that in the tetrahedral complexes, the $d\epsilon$ orbitals of the central atom are bonding, as there are attached orbitals of similar group properties with which they can combine, while the $d\gamma$ orbitals are nonbonding. The reverse was true of octahedral compounds—a result at first a little surprising in view of the isomorphism of the groups T_d and O_h. This reversal was also deduced by Mulliken[8] from the geometrical study of the way the central wave functions "overlap."

It will be observed that if eight atoms are attached, their full bonding power is not utilized unless one includes f wave functions for the central atom, since the representation B_{2u} is not included in s, p, or d. Now f wave functions usually have too high energy to be normally available, or else are so sequestered in the interior of the atom as to be of no value for bonding because of small overlapping. Even if eight atoms are attached at the corners of a cube, central f wave functions must be included in order to realize all possible bonding partnerships, for results always true of tetragonal symmetry surely apply to cubic symmetry, which is a special case of the latter. On the other hand, no f functions are needed for six atoms attached either octahedrally or at the corners of a trigonal prism. We thus have an indication of why it is that coordination numbers of six are common in nature, while those of eight are rare.

METHOD OF DIRECTED ELECTRON PAIRS

We now turn to the method of Pauling and Slater. Here the procedure is to use hybridized

[8] R. S. Mulliken, Phys. Rev. **40**, 55 (1932).

[9] In adapting Table I to the case C_{3v}, the following irregularity, however, is to be noted: one must replace A_1', A_1'', A_2', A_2'', respectively, by A_1, A_2, A_2, A_1 rather than by A_1, A_1, A_2, A_2 as one would guess.

[10] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 219 (1935).

central orbitals, i.e., linear combinations of orbitals of different azimuthal quantum number, in such a way that the resulting central wave function projects out especially in some one direction in space, and so is adapted to form an electron pair with one particular attached atom. Thus for tetrahedral compounds Pauling and Slater[1] use wave functions which are linear combinations of s and p, or alternatively as Pauling[1] shows, of s and $d\epsilon$ wave functions. For octahedral compounds, Pauling finds that $sp^3d\gamma^2$ combinations are appropriate, and $sp^2d\gamma$ for tetragonal. Hultgren[11] proves that eight atoms cannot be attached (at least symmetrically) by means of unidirectional electron pair bonds formed from s, p, and d wave functions. Incidentally, the present paper shows that sp^3d^3f functions are needed to hold eight atoms.[12] It will be noted that the wave functions involved in the Pauling unidirectional linear combinations are precisely those which are bonding in the method of molecular orbitals. For example, Pauling, like Mulliken, makes no use of $d\gamma$ orbitals for tetrahedral compounds, or of $d\epsilon$ for octahedral. Such coincidences have hitherto appeared something of a mystery, but an immediate explanation, as follows, is furnished by group theory.

In the Pauling-Slater theory, one desires the central wave functions to possess unilateral directional properties so as to be correlated with one particular attached atom. Hence the P-S central functions must have the same transformation properties as do those ψ_i of the attached atoms before linear combinations of the latter are taken. Thus the problem of finding the linear combinations of the central orbitals which exhibit the proper directional properties is simply the reverse of finding the proper linear combinations of the attached orbitals in the Mulliken procedure. The difference is only that in the P-S theory, the linear combinations are in the central rather than attached portion, and their construction corresponds to transformation from an irreducible representation to a reducible one, of structure similar to that belonging to the original ψ_i's, rather than to the inverse transformation.[13] Clearly, the same irreducible representations are needed in the construction of a given reducible representation as those contained in the resolution of the latter into its irreducible parts. Pauling has obviously shown considerable ingenuity in constructing his wave functions without using the status in terms of group theory.

Generality of the Results

The argument underlying Table I, etc., ostensibly assumed that the molecular orbital be expressible as a linear combination of atomic orbitals, but is readily seen to be still applicable provided only that the charge cloud of any attached orbital be symmetric about the line joining the given attached atom to the central one. Hence the atomic orbitals can be of what James calls the flexible type, i.e., contain parameters which can be varied in the Ritz method, and which allow for the fact that chemical combination distorts the atomic orbitals from what they would be in the free condition. This admission of flexibility is fortunate, for it is well known that it is a bad quantitative approximation[5] to express a molecular orbital as a linear combination of undistorted atomic orbitals. The Ritz variational problem is, of course, to be of the 1 rather than n electron type, so that the generality in our analysis by means of molecular orbitals is roughly comparable with that in the Hartree method.

One thing which the preceding analysis does not do is to tell us what is the best arrangement of atoms in case the symmetry group does not uniquely determine this arrangement. For instance, by examining the overlapping of wave functions, Hultgren[11] finds that when six atoms are attached at the corners of a trigonal prism, the binding is firmest if the sides of the prism are square. This fact cannot, however, be inferred from our group theory considerations, as there are no additional elements of symmetry when the sides are square rather than rectangular.

[11] R. Hultgren, Phys. Rev. **40**, 891 (1932).

[12] Similar conclusions on the type of bonds necessary to attach eight atoms have also been obtained in unpublished work of R. S. Mulliken.

[13] This transformation has been explicitly given by the writer in the case of methane (J. Chem. Phys. **1**, 177 (1933)), but he did not discuss its group-theoretical significance.

Valence Strength and the Magnetism of Complex Salts

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(Received October 7, 1935)

Certain complex salts, notably ferro- and ferricyanides, have susceptibilities much lower than those predicted by the Bose-Stoner "spin only" formula. The first interpretation was that given by Pauling on the basis of (I) directed wave functions. In the present paper it is shown that alternative explanations are possible with (II) the crystalline potential model of Schlapp and Penney, or with (III) Mulliken's method of molecular orbitals. In any of the theories, the interatomic forces, if sufficiently large, will disrupt the Russell-Saunders coupling, and make the deepest state have a smaller spin, and hence smaller susceptibility, than that given by the Hund rule. This situation is not to be confused with that in normal paramagnetic salts, such as sulphates or fluorides, where only the spin-orbit coupling is destroyed. The similarity of the predictions with all three theories is comforting, since any one method in valence usually involves rather questionable approximations. Because of this similarity, a preference between the theories cannot be established merely from ability to interpret the anomalously low magnetism of the cyanides. Covalent bonds, as in cyanides, seem to be more effective in suppressing magnetism than are ionic ones, as in fluorides, but so far the evidence to this effect is empirical rather than theoretical.

IN most salts of the iron group, the susceptibility has approximately the value

$$\chi = 4N\beta^2 S(S+1)/3kT, \qquad (1)$$

where β is the Bohr magneton $he/4\pi mc$, and where the spin S has the value given by the Hund rule that the ground state is that of maximum multiplicity compatible with the Pauli principle. Formula (1) was suggested by Bose and Stoner. The theoretical explanation has been known for some time,[1] and is that the crystalline field is so strong as to destroy the coupling of the spin angular momentum S and orbital angular momentum L to a quantized resultant J. It can be shown that with such an "electric Paschen-Back effect," the orbital magnetism is largely quenched, and the susceptibility has nearly the value (1).

There are, however, certain compounds of elements of the iron group, notably iron cyanides and the various cobaltammines, for which the susceptibility has a value very much lower than that given by (1). In fact, these compounds are diamagnetic if they involve a complex ion containing an even number of electrons (e.g., $Fe(CN)_6^{4-}$), or have a susceptibility of an order of magnitude corresponding to one free spin, i.e., to $S=\frac{1}{2}$ in (1), if this number is odd (e.g., $Fe(CN)_6^{3-}$). The first specific model accounting for this behavior was given by Pauling,[2] but the explanation may be couched in more general language as follows: the interatomic forces are so very large as to destroy not merely the spin-orbit but also the Russell-Saunders coupling, and make the deepest state that of lowest possible spin rather than of maximum spin as given by the Hund rule.[3] Large spin would be an advantage as far as a free atom is concerned, but the point which we wish to make is that the interatomic energy is decreased by lowering the total spin regardless of whether one makes the calculation in any of three ways:

(I) the directed electron pair bond, sometimes called the Heitler-London-Pauling-Slater approximation,

(II) the method of crystalline fields, particularly adapted to ideally ionic compounds, and

(III) Mulliken's method of molecular orbitals.[4]

There is thus a formal similarity between the results of various approaches, in many respects paralleling that on the subject of directional valence stressed in the preceding paper. The cyanide anomalies have been previously interpreted only on the basis of I, although Mulliken[4] did state that magnetic behavior might often be equally intelligible with the mechanism III.

The particular examples which we shall consider are compounds in which the central or

[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Chap. XI.

[2] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).

[3] For this rule see, for instance, Pauling and Goudsmit, *The Structure of Line Spectra*, p. 165.

[4] R. S. Mulliken, Phys. Rev. **40**, 55 (1932).

paramagnetic atom has a coordination number of six resulting from six neighboring atoms or ions octahedrally arranged. The clusters $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, FeF_6^{3-}, in $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $(NH_4)_3FeF_6$, respectively, are structures of this character. It is not necessary that the crystal as a whole have cubic symmetry. For instance, $K_3Fe(CN)_6$ is monoclinic. From these examples we trust it will be sufficiently clear how the similarity between the various methods is demonstrated in other cases.

The deepest state of the Fe^{+++} ion is a ^6S term, and indeed the observed susceptibility[5] of $(NH_4)_3FeF_6$ approximately equals that given by (1) with $S=5/2$. The susceptibility[6] of $K_3Fe(CN)_6$, however, is much nearer the value given by (1) with $S=\frac{1}{2}$. The interatomic forces should thus be relatively more important in the cyanides than in the fluorides, and it is, in fact, known that the former are firmer compounds than the latter.

I. The Method of Directed Electron Pair Bonds

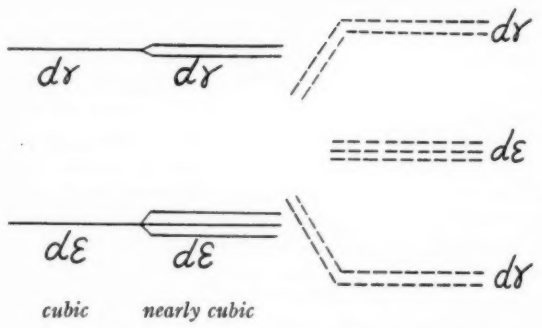
The magnetic behavior of $Fe(CN)_6^{3-}$ is explained by Pauling on the basis of the structure $Fe^{3-}(CN)_6$. This model need not be literally true, but is taken to be sufficiently typical, i.e., a sufficiently common phase in the resonance through various stages of polarity, to serve for purposes of discussion. According to Pauling,[2] the Fe^{3-} ion attaches its six atoms of coordination by means of six $sp^3d\gamma^2$ electron pair bonds. These six bonds consume the $4s$, $4p$, and $d\gamma$ states,[7] and house six electrons of Fe^{3-}. (Only one electron can be assigned to a state of the central atom which is used for bonding purposes; for if a state houses two electrons, their spins compensate each other, and they are not free to form electron pair bonds with outside atoms.) The Fe^{3-} ion has 11 electrons in all to house (apart from completed inner shells). The five electrons not absorbed by the electron pair bonds can only be accommodated in the three $3d\epsilon$ states. Thus two of these states will be filled twice. The electrons which are thus "doubled up" must have their spins antiparallel because of the Pauli principle, and hence make no contribution to the susceptibility. The fifth electron, however, has a free spin, so that the susceptibility should be given approximately by (1) with $S=\frac{1}{2}$ provided one can overlook orbital contributions to the susceptibility. Actually they are not negligible, as Howard shows in the next paper. In $Fe(CN)_6^{4-}$, there is an additional electron to house, so that the fifth electron loses its private state, and there can only be diamagnetism, in agreement with experiment.

II. The Method of the Crystalline Potential

The simplest model for explaining the varying magnetic properties is that used with success by Penney and Schlapp[8] primarily on hydrated sulphates of the rare earth and iron groups. The basic assumption is that the effect of neighboring atoms can be represented by means of a static potential. One may distinguish between three cases depending on the strength of the crystalline field: (a) the field is so weak that the inner quantum number J has a meaning (b) it is so large as to prevent J, but not L or S from being a good quantum number, and (c) it is still more powerful, and able to destroy Russell-Saunders coupling, i.e., the compounding of the individual l's to a resultant L, so that L loses its validity as a quantum number. Cases (a) and (b) are those studied by Penney and Schlapp, (a) being characteristic of the rare earths, and (b) of the hydrated sulphates of the iron group. We shall now show that (c) furnishes an explanation of the behavior of the cyanides and other salts having abnormally low susceptibilities.

In the compounds in which we are at present interested, the crystalline field is of dominantly cubic symmetry. In a field of this symmetry type, it can be shown by means of group theory,[9] or otherwise, that a d electron has the Stark pattern shown in Fig. 1. The separation of the

[5] E. Cotton-Feytis, Ann. Chim. **4**, 9 (1925).
[6] Cf. for instance, L. C. Jackson, Proc. Roy. Soc. **A140**, 695 (1933).
[7] For explanation of the notation $d\gamma$, $d\epsilon$ see Eqs. (5)–(6) of the preceding paper in this issue.
[8] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); R. Schlapp and W. G. Penney, ibid. **42**, 666 (1932); O. Jordahl, ibid. **45**, 87 (1934); R. Janes, ibid. **48**, 78 (1935).
[9] See, for instance, H. Bethe, Ann. d. Physik **3**, 143 (1929).



Splitting in method of crystalline potentials

FIG. 1.

Splitting in method of molecular orbitals

FIG. 2.

levels which branch out from a common origin on the left is, by hypothesis, comparatively small, and owes its existence to the deviations of the field from perfect cubic symmetry. Do not confuse Fig. 1, which is for one electron, and the closely related crystalline Stark diagrams given by Penney, Schlapp, and Van Vleck for whole atoms in which the electrons are space quantized collectively rather than individually. Fig. 1 is right side up, as Gorter[10] shows, so long as the negative ions surrounding the paramagnetic cation are octahedrally arranged. Fig. 1 should be inverted in case the coordination number is four rather than six, i.e., the symmetry tetrahedral rather than octahedral. Now if we assume the conventional polar structure $Fe^{+++}(CN^{-})_6$, the Fe^{+++} ion has five electrons outside closed shells, and there are five electrons to be housed in the various states of Fig. 1. Clearly the deepest energy is obtained by assigning the five electrons to the three components of $d\epsilon$. Then all the electrons but one double up, and there is only one free spin, while in $Fe^{++}(CN^{-})_6$ there would be no free spin. Thus with a sufficiently large field to make individual space quantization a good approximation, the deepest state is quite different from that ^6S given by the Hund rule.

It is interesting to note the significance of the state $d^5\ ^6S$ in terms of Fig. 1. Usually Russell-Saunders coupling involves collective quantization in such a way as not to permit any simple interpretation in terms of a one-electron diagram such as Fig. 1. However, when the spin quantum number equals half the number of electrons, as in $d^5\ ^6S$, the spins are all mutually parallel. Such an alignment is possible only if each electron has its own private orbital. Hence a state of the configuration d^5 with $S=5/2$ involves one electron in each of the five levels of Fig. 1. This distribution has an invariant significance (one to a state) regardless of how the axis of space quantization is chosen. Hence this state must be an S state, as is also proved by other means and as is reflected in the high magnetic isotropy of manganous and ferric salts of the sulphate variety. When, however, one has the cyanide case, there are three different ways in which the five electrons may be distributed among $d\epsilon$, since the private orbital may be the lower, middle, or upper component of $d\epsilon$. True cubic symmetry is achieved only if the three components are populated equally. Hence $K_3Fe(CN)_6$ can exhibit a high degree of magnetic anisotropy. This point is studied quantitatively by J. Howard in the next paper.

As we have seen, the energy due to the crystalline field is lowest when the Hund rule is broken down. However, the internal energy of the Fe^{+++} ion is lower with $S=5/2$ than with $S=\frac{1}{2}$. (This is the meaning of the Hund rule.) Thus whether the total internal plus external energy is lower or higher for $S=5/2$ than for $S=\frac{1}{2}$ is a question purely of the size of the crystalline potential relative to the strength of the Russell-Saunders coupling. The fact that both cases are actually realized suggests that the two energies are of the same order of magnitude, and such indeed appears to be the case. The crystalline fields deduced by Schlapp, Penney, Jordahl, and Janes[8] for the hydrated sulphates usually amount to about 3 volts.[11]

[10] C. J. Gorter, Phys. Rev. **42**, 437 (1932).

[11] In Cr^{+++} an over-all splitting of about 8 volts is obtained by Schlapp and Penney, a value which seems unduly high and out of line with their other results. As they intimate, the explanation of this discrepancy is probably that in Cr^{+++}, the computation of the splitting is unusually sensitive to small experimental errors in the determination of the absolute value of the susceptibility because the latter has very nearly the "spin-only" value in this particular ion. Schlapp and Penney employed the Leiden data on chrome alum. It is interesting to note that a splitting (3 volts) of about the usual size is yielded by Janes'[8] recent measurements on $K_3Cr(SCN)_6 4H_2O$. Incidentally, the separation 17,200 cm^{-1} which Janes obtains in cupric salts relates to the over-all splitting, rather to the constant D as stated in his article, and so is not unreasonable.

The strength of the Russell-Saunders coupling is measured by the separation of the various levels arising from the configuration d^5 in the free ion. Spectroscopic data indicate that this separation amounts to only about 4 or 5 volts.[12] Hence the crystalline field would not have to be much larger than in the examples studied by Schlapp and Penney in order to overpower the Russell-Saunders coupling,[13] and so it is plausible that this situation is realized in the cyanides.

Even in the case studied by Schlapp and Penney, labeled (b) above, the separation between the various states of the configuration $3d^x$ is not larger than the crystalline potential. Consequently one naturally wonders whether they were justified in neglecting matrix elements between states of different L but similar S belonging to the same configuration. Neglect of matrix elements between states differing both in L and S is legitimate if the intervals between such states are large compared with the spin-orbit interaction, i.e., with multiplet widths. This condition is practically always fulfilled. In Fe^{+++} or Mn^{++} there can be no question of rigor, since the configuration d^5 has only one sextet state. Also in Cr^{++} or Fe^{++} (d^4 or d^6) there is only one quintet, while in Cu^{++} (d^9) there is only one state of any character, a doublet. In Cr^{+++} or Co^{++}, however, the states of highest multiplicity are ^4F and ^4P, while in Ni^{++}, they are ^3F and ^3P. The separation between these two states is only about 2 volts[14] in either Co^{++} or Ni^{++}. Spedding[15] criticizes the work of Schlapp and Penney on the ground that they do not consider the perturbing effect of ^3P in their calculations of the ^3F state of Ni^{++}, or of ^4P on the ^4F of Cr^{+++}, Co^{++}. However, Spedding has overlooked the fact that in Cr^{+++} or Ni^{++} the Stark component of the F level which is important for the magnetic calculations is that which belongs to the representation A_2[16] of the cubic group. On the other hand, ^3P or ^4P belongs to the representation T_1, and so is incapable of perturbing A_2, if the field is really cubic. This statement is not quite true when one allows for the fact that the spin-orbit distortion makes the symmetry different from that characteristic of orbit alone. In other words, one ought rigorously to consider the irreducible transformation properties of the spin-orbit rather than just orbital wave functions. However, the spin-orbit distortion is subordinate, and so the perturbation due to this cause is negligible. Furthermore the Stark component A_2 of ^3F or ^4F involves different rhombic representations than do ^3P or ^4P, and so cannot be perturbed by the latter even when one considers the deviations from cubic symmetry, as long as rhombic symmetry is preserved. Hence Schlapp and Penney's conclusions on the nearly perfect magnetic isotropy of Ni^{++}, Cr^{++} and their close conformity to (1), are unaffected. In the case of Co^{++}, the ground level is the Stark component T_1 of $d^7\,{}^4F$, and can be perturbed by $d^7\,{}^4P$. We hope to study this effect later more fully. In Co^{++}, anyway, the agreement which Schlapp and Penney obtained with experiment was qualitative rather than quantitative. Rough preliminary examination suggests that it will probably be improved by considering the perturbation by ^4P. Hence, we conclude that all the vital features of Schlapp and Penney's calculations are unaffected by considering the incipient breakdown of Russell-Saunders coupling, and that in Co^{++} the quantitative agreement may actually be bettered.

III. The Method of Molecular Orbitals

This method differs from the crystalline field procedure II in that the structural unit for the wave function is the whole complex ion (e.g., $Fe(CN)_6^{3-}$) rather than the single central atom. Both II and III utilize one-electron wave functions, and so group theory based on symmetry properties can still be used to obtain information about the character of the levels. However, there is the difference that if a central orbital is bonding, a given representation appears more often than in method II because of the fact that, in the language of the preceding paper, there are both central and attached orbitals belonging to the same irreducible representation. The proper

[12] Spectroscopic data are not available on the Fe^{+++} ion. However, the separation of the various terms belonging to the configuration d^5 in Fe^{+++} should be somewhat greater than (probably a little less than double) the corresponding separations in the homologous ion Cr^+, and the interval $d^5\,{}^6S-d^5\,{}^4G$, for instance, is known to be 2.5 volts in Cr^+.

[13] Unfortunately it does not appear possible to estimate directly from theoretical considerations the crystalline splitting to be expected even with an ideal ionic structure and assumed interatomic separations obtained from Pauling's atomic radii. So one can only deduce the splittings empirically from the magnetic data. The difficulty is that one does not know well enough the effective charge Z to be used in computing the d wave functions. Clearly Z should be somewhat greater than 4, the value corresponding to perfect screening, and somewhat less than the effective charge Z_{ip} deduced from ionization potentials, as the value of Z to be used in computing $\overline{r^4}$ etc. is less than that involved in $\overline{1/r}$. Extrapolated spectroscopic data indicate that Z_{ip} is about 6. In unpublished calculations, Howard finds that the interval $d\gamma-d\epsilon$ amounts to 4 volts if $Z=4$ and to 1 volt if $Z=6$, provided the further assumptions are made that the distance Fe−F is 1.91A, and that the F^- ions act like point charges.

[14] The intervals $d^7\,{}^4F-d^7\,{}^4P$ of Co^{++} and $d^8\,{}^3F-d^8\,{}^3P$ of Ni^{++} have not been observed directly, but probably do not differ greatly from the intervals $d^7(^4F)4s^2-d^7(^4P)4s^2$ of Co I, and $d^8(^3F)4s^2-d^8(^3P)4s^2$ of Ni I, respectively. These latter intervals are known and are both 1.9 volts. That the addition of the $4s$ electrons does not change too materially the separations of the core states is indicated, for instance, by the fact that the frequency difference $d^4(^3F)4s\,{}^4F-d^4(^3G)4s\,{}^4G$ in Cr II deviates only 4 percent from the difference $d^4\,{}^3F-d^4\,{}^3G$ in Cr III (see Bacher and Goudsmit's tables).

[15] F. H. Spedding and G. C. Nutting, J. Chem. Phys. **2**, 421 (1935).

[16] For explanation of the notation for the group representations see R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

linear combination of such central and attached orbitals is found by solving a secular equation. In the case of the octahedral group, the wave functions belonging to the irreducible representation E_g are

$$\psi(E_g)=\alpha\psi(3d\gamma_1)+(1-\alpha^2)^{\frac{1}{2}}(1/12)^{\frac{1}{2}}(2\psi_3+2\psi_6-\psi_1-\psi_4-\psi_2-\psi_5), \quad (2a)$$

$$\psi''(E_g)=(1-\alpha^2)^{\frac{1}{2}}\psi(3d\gamma_1)-\alpha(1/12)^{\frac{1}{2}}(2\psi_3+2\psi_6-\psi_1-\psi_4-\psi_2-\psi_5), \quad (2b)$$

$$\psi'(E_g)=\alpha\psi(3d\gamma_2)+(1-\alpha^2)^{\frac{1}{2}}\tfrac{1}{2}(\psi_1+\psi_4-\psi_2-\psi_5), \quad (3a)$$

$$\psi'''(E_g)=(1-\alpha^2)^{\frac{1}{2}}\psi(3d\gamma_2)-\alpha\tfrac{1}{2}(\psi_1+\psi_4-\psi_2-\psi_5), \quad (3b)$$

where the wave function of attached atom i is denoted by ψ_i, and the explicit forms of the central wave functions $\psi(d\gamma)$ are as given in Eqs. (5)–(6) of the preceding paper. Attached atoms 1, 4 are supposed located on the x axis; 2, 5 on the y; and 3, 6 on the z. The value of α is determined, at least in principle by solving a secular equation. Similarly, the wave functions corresponding to A_{1g} and T_{1u} are

$$\psi(A_{1g})=\beta\psi(4s)+(1-\beta^2)^{\frac{1}{2}}(\tfrac{1}{6})^{\frac{1}{2}}(\psi_1+\psi_2+\psi_3+\psi_4+\psi_5+\psi_6), \quad (4a)$$

$$\psi(T_{1u})=\gamma\psi(4p\sigma_x)+(1-\gamma^2)^{\frac{1}{2}}(\tfrac{1}{2})^{\frac{1}{2}}(\psi_1-\psi_4), \quad (5a)$$

$$\psi'(T_{1u})=\gamma\psi(4p\sigma_y)+(1-\gamma^2)^{\frac{1}{2}}(\tfrac{1}{2})^{\frac{1}{2}}(\psi_2-\psi_5), \quad (6a)$$

$$\psi''(T_{1u})=\gamma\psi(4p\sigma_z)+(1-\gamma^2)^{\frac{1}{2}}(\tfrac{1}{2})^{\frac{1}{2}}(\psi_3-\psi_6), \quad (7a)$$

together with four other wave functions (4b)–(7b) which are similar except that β, $(1-\beta^2)^{\frac{1}{2}}$ are replaced, respectively, by $(1-\beta^2)^{\frac{1}{2}}$, $-\beta$, etc. The notation $p\sigma_x$ means a p state with $m_l=0$ when the quantization is relative to the x axis. The basic theoretical principles underlying the construction of wave functions such as (2)–(7) are outlined in the preceding article.[17]

The lower roots of the quadratic secular equations associated with (2)–(7) represent lower energy than for the free atom, i.e., are bonding levels, while the upper roots give higher energy than for the free atoms, i.e., are antibonding. The $d\epsilon$ wave functions are nonbonding, as shown in the previous paper. The situation is illustrated in Fig. 2. All these statements on the positions of the levels are surely true as long as the important term for bonding is the so-called Hund resonance integral, which is the off-diagonal matrix element connecting the central and attached portions. Since diagonal sums are unaffected by the addition of off-diagonal elements, it follows that the sum of the two roots of the quadratic must equal an energy level of the free central atom, plus one of the attached atom. Hence if one root is lowered in virtue of the resonance integral, the other must be raised.

Let us now discuss the case of $Fe(CN)_6^{3-}$. We can consider each CN radical as contributing one electron (*viz.*, the electron which corresponds to a $2p\sigma$ wave function directed towards the central atom). There are thus 17 electrons in all to house (apart from completed inner shells). Twelve electrons can be housed in the lower roots of the secular equations associated with (2)–(7), since the Pauli principle allows two electrons to an orbital state. The remaining five electrons are then to be accommodated in the three nonbonding, i.e., purely central $d\epsilon$ orbitals, which are preferable to antibonding states. One, and only one, of these five electrons can have a private orbital, and so only one spin contributes to the susceptibility. With $Fe(CN)_6^{4-}$, the last six electrons are snugly accommodated in the three $d\epsilon$ levels, and so there is diamagnetism. Of course, if the bonding action is weak enough, several electrons may prefer to occupy private orbitals, even though antibonding, in order to secure large spin and low internal energy for the central atom. This is a refinement not included in the crude forms of the method of molecular orbitals, for it is the interelectronic exchange energy, not incorporated in the one-electron problem, which is lowered by making the spins parallel. Thus we see that, as in the other methods, the susceptibility will have the low values characteristic of the cyanides only if the bonding action is larger than the Russell-Saunders structure of the central atom.

Comparison of the Various Methods

We have now seen that all three descriptions are capable of explaining the anomalously low

[17] Cf. also J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 218–222 (1935).

magnetism of the cyanides. The question naturally arises as to which corresponds the closest to reality. It seems to us that in the cyanides one must decide in favor of III or possibly I. One reason is that method III is the most general, since it is noncommittal on the amount of polarity, which can be anything between $Fe^{3+}(CN^-)_6$ and $Fe^{0-}(CN^+)_6$, depending on the size of the coefficients α, β, γ. In fact, II can be regarded as a special case of III, wherein these coefficients are zero and the CN orbitals have lower energies than those of the central atom, so that the twelve electrons digested by (2–7) are located on the CN radicals. Method I is also to a certain extent a special case of III, corresponding to

$$\alpha=\beta=\gamma=\sqrt{\tfrac{1}{2}}, \tag{8}$$

but we have seen in the preceding paper that in any event I differs from III in assuming localized or unidirectional bonds. Eq. (8) may be regarded as the condition for ideal covalency, as when it is satisfied, the twelve bonding electrons spend equal amounts of time on the $(CN)_6$ group and on the central atom. The actual behavior is not as extreme as in (8), for the structure $Fe^{3-}(CN)_6$ given by (8) requires too much negative charge on the Fe ion, as mentioned at the beginning of the preceding paper.

A decision between II and III is furnished by the fact that $(NH_4)_3FeF_6$ obeys the ordinary formula (1), and so has a much higher magnetism than $K_3Fe(CN)_6$. Now it is known from other evidence[18] that $(NH_4)_3FeF_6$ is much more polar in its structure, i.e., more nearly $(NH_4^+)_3Fe^{3+}(F^-)_6$, than is $K_3Fe(CN)_6$. With the method of the crystalline potential, the fields responsible for the Stark splitting are those due to the negative charges surrounding the paramagnetic cation. Hence if method II were always applicable, the quenching of magnetism would be more complete in the fluoride than in the cyanide, contrary to experiment. On the other hand, in the method III of molecular orbitals, the strength of the bond or separation of the levels stands in no immediate relation to the amount of polarity, and it is perfectly possible to have a covalent structure quench magnetism more completely than an ionic one. In fact, if the resonance integrals are the determining factor in chemical bonds, one comes nearer to (8) the greater the interatomic forces available to suppress the magnetism.

Pauling has argued that the suppression of magnetism is evidence in favor of the electron pair mechanism I in $Fe(CN)_6^{3-}$. However, we have seen that II or III can also be effective in quenching magnetism, so that it does not seem possible directly to infer the bond type from magnetic behavior. We agree with Pauling that covalent bonds are more effective in destroying magnetism than ionic, but the reasoning by which we reach this conclusion is somewhat different and is based on the empirical comparison of $(NH_4)_3FeF_6$ and $K_3Fe(CN)_6$ made above. Once it has been established empirically in a few cases that covalent bonds destroy magnetism more than ionic, one is probably justified in extrapolating to other cases, and supposing the bonds to be covalent when most of the magnetism has been destroyed.

If method III is to be preferred to II, the calculations of Schlapp and Penney,[8] based ostensibly on II, must be given a somewhat different interpretation than previously. They by no means lose applicability, for they are based largely on the symmetry group properties, and so retain practically as much significance with III as with II, except that the size of the crystalline potential is not to be taken too literally. The splittings of a few volts may now relate to the magnitude of the Hund resonance integrals rather than of the crystalline potential, but remain comparable to the Russell-Saunders structure, making it still reasonable that one should sometimes have the cyanide behavior and sometimes the sulphate.

One feature which is common to methods I, II, III is that nickel salts should have a susceptibility corresponding to $S=1$ rather than to $S=0$ in (1) even if the cubic splitting is large compared with the Russell-Saunders structure. This statement is true if the grouping about the nickel ion is either tetrahedral or octahedral. The demonstration has been given by Pauling[2] with mechanism I and by Van Vleck and Sherman[17] with III. If II is used, one has only to note that Ni^{++} has two more electrons than Fe^{++}, so

[18] L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932); Pauling and Huggins, reference 2.

that there are eight rather than six electrons to be housed in the five levels of Fig. 1. Hence regardless of whether Fig. 1 is upright or inverted, two electrons can have private orbitals without materially diminishing the energy, provided the rhombic splitting in Fig. 1 is small. To explain the observed diamagnetism of $K_2Ni(CN)_4$, one is thus led to predict a square (tetragonal) rather than tetrahedral configuration for the $Ni(CN)_4^{--}$ ion. This prediction is confirmed by x-ray measurements[19] on $BaNi(CN)_4 4H_2O$. On the other hand, $Ni(NH_3)_4SO_4$ is paramagnetic, and this fact suggests that there may be a tetrahedral structure for the group $(NH_3)_4$.

Our arguments to explain the diamagnetism of $K_4Fe(CN)_6$ apply equally well to diamagnetic cobaltic compounds such as the cobaltammines, since Co^{+++} is isoelectronic with Fe^{++}. The writer has shown elsewhere[20] that if the coordination number is six, and if (1) is valid (the sulphate rather than cyanide case), cobaltous compounds should show marked anisotropy and deviations from Curie's law, while the reverse should be true of nickel ones. If the coordination number is four, the roles of cobalt and nickel should be interchanged. Blue and pink cobaltous salts are supposed to involve coordination numbers of four and six, respectively.[21] It would therefore be interesting to see if one could prepare a blue cobaltous salt conforming closely to Curie's law. Attempts of R. B. Janes to do this have so far proved unsuccessful. The explanation may be either that the magnetic dilution is insufficient, so that the exchange forces between paramagnetic ions complicate the temperature dependence, or else that one is in the critical transition region wherein the mechanism for suppressing the magnetism below (1) just comes into play. In the latter event both states with $S=\frac{1}{2}$ and $S=3/2$ are populated, and the temperature variation will not be simple.

In conclusion, we may say that it should be regarded as reassuring and significant that all three mechanisms I, II, III permit a rational understanding of magnetism lower than that given by (1) and the Hund rule. Since none of the methods of approximation can be regarded as satisfactory from a quantitative standpoint, a property which is common to all three must be regarded as on a much firmer basis than if it is characteristic only of one approach.

The writer wishes to thank Mr. John Howard for interesting and valuable discussions.

[19] H. Brasseur, A. de Rassenfoss and J. Piérard, Zeits. f. Krist. **88**, 210 (1934).

[20] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932). In this connection see reference 10 regarding the relation between coordination number and the sign of the crystalline field.

[21] R. Hill and O. R. Howell, Phil. Mag. **48**, 833 (1924).

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

The Principal Magnetic Susceptibilities of $K_3Fe(CN)_6$

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(Received October 7, 1935)

The magnitudes, anisotropy and temperature dependence of the principal magnetic susceptibilities of $K_3Fe(CN)_6$ are calculated by the method of crystalline potentials, and prove to be in good agreement with experiment. The assumption is made that the interatomic forces in the $Fe(CN)_6^{---}$ complex destroy Russell-Saunders coupling. This results in a susceptibility corresponding to *one* free electron spin with a contribution, except at very low temperatures, from the unquenched orbital angular momentum. The effect of the latter is sufficient to make the susceptibility at room temperature almost twice as large as the value which would be obtained if the spin alone were considered. The superposition of a small rhombic crystalline field suffices to produce the large observed magnetic anisotropy. The behavior of the susceptibility of $K_3Fe(CN)_6$ is in sharp contrast to the higher effective magneton numbers and magnetic isotropy of many ferric compounds, such as the sulphates. In these the ground state of Fe^{+++} is the normal state of the free ion, namely a ^6S state, so that five spins contribute to the susceptibility. Although the calculations ostensibly use the method of crystalline potentials, they are really based on general group properties and so apply even if the bonds in the cyanide are covalent, as they probably are, rather than ionic.

Introduction

THE magnetic measurements made by Jackson[1] on single crystals of $K_3Fe(CN)_6$ in the temperature range 75°–290°K reveal, in addition to the abnormally low susceptibility reported by other investigators, a remarkable anisotropy amounting to almost 100 percent at low temperatures. Compounds of ferric iron in general exhibit a high degree of magnetic isotropy and a mean susceptibility corresponding to a spin of 5/2. This latter behavior is to be expected if the Fe^{+++} ion in the crystal is in the ^6S state, which is the ground state of the free ion.[2] In the second of the foregoing articles[3] Van Vleck has demonstrated how the low susceptibility and magnetic anisotropy of $K_3Fe(CN)_6$ may be explained upon the assumption that the interatomic forces are sufficiently powerful to destroy Russell-Saunders coupling.[4] A quantitative study of the susceptibility of this compound, based on this assumption, is presented in the present paper.

General Procedure

The principal molar susceptibilities may be calculated from the expression[5]

$$\chi=\frac{L\sum_n[(W_n^{(1)2}/kT)-2W_n^{(2)}]e^{-W_n^0/kT}}{\sum_n e^{-W_n^0/kT}}. \quad (1)$$

Here L is Avogadro's number. The other constants are the coefficients of an expansion of the energy W_n in powers of the applied magnetic field $\mathfrak{H}$

$$W_n=W_n^0+W_n^{(1)}\mathfrak{H}+W_n^{(2)}\mathfrak{H}^2+\cdots. \quad (2)$$

The summation is over all states of the system. In the so-called method of crystalline potentials[6] this system is taken to be the magnetic ion subject to the constant ionic field of its neighbors in the crystal. The problem of finding the susceptibility is thus reduced simply to that of determining the relative energy levels W_n^0 of the magnetic ion in a crystalline field of a certain symmetry and finally the energies in the form (2) when a magnetic field is superposed. This is accomplished by means of a perturbation calculation in which the unperturbed system has the type of coupling most appropriate to the size of the crystalline field.

For the time being we shall use the language of the method of crystalline potentials and regard the interatomic forces of the $Fe(CN)_6^{---}$ complex as electrostatic. But we shall later see at the conclusion of the paper, that our calculations are independent of the nature of the bonding mechanism assumed.

In the present problem we assume that the coupling of the individual l's to a resultant orbital angular momentum L is destroyed by a large cubic field, which is the dominant portion of the crystalline potential. In this respect our calculations differ from those of Schlapp and Penney,[6] on Cr, Co and Ni compounds, wherein only the spin-orbit interaction is broken down. The unperturbed state of the Fe^{+++} ion in our problem is consequently taken to consist of five non-interacting $3d$ electrons. Under the action of the cubic potential the single d electron level splits into a triply and a doubly degenerate level, which we shall designate $d\epsilon$ and $d\gamma$ respectively.[7] Gorter[8] has shown that in an octahedral complex such as $Fe(CN)_6^{---}$ the triplet will lie lower. We now make the following approximation. We assume that the splitting of the d level is so large that we may neglect contributions to the susceptibility of perturbation matrix elements connecting the triplet and singlet levels. In order to uncouple the individual l's, this splitting must, of course, exceed 3×10^4 cm^{-1}, the approximate separation[9] of different multiplets arising from the d^5 configuration of Fe^{+++}.

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[1] L. C. Jackson, Proc. Roy. Soc. **A140**, 695 (1933).

[2] See J. H. Van Vleck, Phys. Rev. **41**, 208 (1932). For experimental data on the magnetic isotropy of ferric and manganous salts see Jackson, reference 1; Krishnan, Chakravorty and Banerjee, Phil. Trans. Roy. Soc. **232**, 99 (1933); Krishnan and Banerjee, Nature **135**, 873 (1935).

[3] We shall refer to Van Vleck's first and second papers in this issue as V.V. I and V.V. II.

[4] This explanation was first advanced by Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934), footnote 6. See Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); **54**, 988 (1932) for an explanation of the low susceptibility based on the concept of localized orbitals.

[5] See Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Ch. VII.

[6] H. Bethe, Ann. d. Physik **3**, 133 (1929); J. H. Van Vleck, reference 5, Ch. XI; W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); **42**, 666 (1932); O. M. Jordahl, ibid. **45**, 87 (1934).

[7] For the full significance of the terms $d\epsilon$ and $d\gamma$ see Eqs. (5) and (6) of V.V. I.

[8] C. J. Gorter, Phys. Rev. **42**, 437 (1932).

[9] Cf. footnote 12 in V.V. II.

Introducing the electron spin we obtain from the triply degenerate $d\epsilon$ level six single-electron states, among which the five electrons are to be distributed. The energy matrix for this $d\epsilon^5$ configuration is the same as that for a single electron in a $d\epsilon$ state except for a change in the signs of the proportionality factors in the perturbation. The reason for this is that five electrons represent a shortage of one from a complete and hence nonmagnetic group of six electrons in the $d\epsilon^6$ configuration. Consequently, by virtue of our discarding the effect of the $d\gamma$ level, we may carry through the calculation of the energy levels as we would for a one-electron system except for this change in signs. The perturbation may then be written

$$H=[Ax^2+By^2-(A+B)z^2] +A'\mathbf{l}\cdot\mathbf{s}+\mathfrak{H}\beta(m_l+2m_s), \quad (3)$$

where A and B are the coefficients of the quadratic term of a rhombic crystalline potential, which is introduced in order to account for the observed magnetic anisotropy; A' is the coefficient of the spin-orbit coupling; $\mathfrak{H}$ is the applied magnetic field; and β is the value of the Bohr magneton $eh/4\pi mc$. The pattern of energy levels produced by the perturbation (3) for the $d\epsilon^5$ configuration is shown in Fig. 1.

Apparently we have specialized things somewhat in assuming that the rhombic potential is a quadratic function of x, y, z. But this is not really true, as the energy of our system in a rhombic field has three eigenvalues, of which one serves as a trivial additive constant since we are interested only in the relative energies. Hence the full generality of the secular problem arising from the lifting of the cubic degeneracy by a rhombic field is realized by (3), since (3) involves two independent constants, A and B, which determine the relative eigenvalues completely.

Expressions for the Principal Susceptibilities

To calculate the energy values of the system one must diagonalize the secular matrix corresponding to the perturbation (3). The matrix elements are given by Schlapp and Penney and Jordahl.[6] The matrix for the $d\epsilon^5$ configuration is

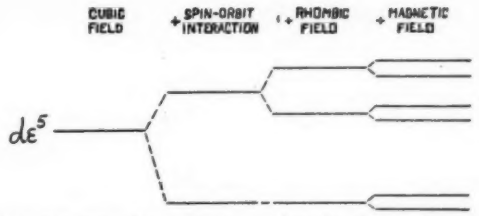

FIG. 1. Pattern of energy levels for the $d\epsilon^5$ configuration.

the same as the sextic corresponding to the irreducible representation Γ_5 given on p. 90 of Jordahl's paper.[10] In the absence of a magnetic field this sextic factors into two identical cubics.

The similar behavior of two of the principal susceptibilities (see Fig. 2) suggests that the rhombic field, which is responsible for magnetic anisotropy, is very nearly axial in symmetry. For convenience the rhombic field in (3) may be written

$$(E+\Delta)x^2+(E-\Delta)y^2-2Ez^2, \quad (4)$$

i.e., we set $A=E+\Delta$ and $B=E-\Delta$. We assume that Δ is small compared with E. In the limit when $\Delta=0$ and the crystalline field has axial symmetry it is possible to solve rigorously the cubic secular equation involving the elements of the axial field and spin-orbit coupling. The complete matrix corresponding to (3) corrected by (4) is then diagonal in all but the elements containing Δ, the deviation from axial symmetry, and the magnetic field $\mathfrak{H}$. A transformation is next made which leaves in off-diagonal positions only terms containing square or higher powers of Δ, which are negligible. Lastly, the effect of the magnetic field on the energy values is computed in the form (2). The final expressions for the relative energy levels are given below. The first set of three energy levels is for the magnetic field parallel to the a and b crystallographic axes.[11] The upper sign corresponds to the a axis,

[10] Jordahl's matrix as a whole is inapplicable to our problem. His system is a d^9 configuration which is one electron short of a completed configuration d^{10}. Our system is a d^5 configuration and only because we have chosen to neglect the effect of the $d\gamma$ level, does it become one electron short of the closed configuration $d\epsilon^6$.

[11] Although $K_3Fe(CN)_6$ has monoclinic symmetry the deviation from orthorhombic symmetry is very slight ($\beta=90°\,6'$). Consequently the crystallographic axes may be considered to coincide with the Cartesian axes along which the magnetic field is taken in the calculation. The susceptibilities which we calculate are for the magnetic field in the direction of these axes, whereas the experimental data with which the susceptibilities are compared are given for the magnetic field along the principal magnetic axes of the

the lower sign to the b axis. The second set of energy levels is for the field along the c axis.

$$W_{\mathrm{I}}^{a,b}=\frac{3m}{2}+\frac{u}{\lambda\zeta}\left(-2n\pm\frac{4w\xi}{3}\right)K+\frac{1}{3\lambda}\left\{-\frac{4u^2(u+v)^2}{\lambda^2\delta\zeta}+\frac{4u^2}{m\zeta}\pm\frac{(u+v)(\xi^{-1}+\xi)w}{3\lambda^2}\pm\frac{16u^2w}{3m\lambda\zeta}\left[\frac{n\xi}{\zeta}+\frac{u+v}{\delta\xi}\right]\right\}K^2,$$

$$W_{\mathrm{II}}^{a,b}=\frac{3p}{2}+\frac{u}{\lambda\delta}\left(-2q\pm\frac{4w}{3\xi}\right)K+\frac{1}{3\lambda}\left\{+\frac{4u^2(u+v)^2}{\lambda^2\delta\zeta}+\frac{4u^2}{\rho\delta}\mp\frac{(u+v)(\xi^{-1}+\xi)w}{3\lambda^2}\pm\frac{16u^2w}{3p\lambda\delta}\left[\frac{q}{\delta\xi}+\frac{(u+v)\xi}{\zeta}\right]\right\}K^2,$$

$$W_{\mathrm{III}}^{a,b}=\mp\frac{4uw}{3\lambda}\left(\frac{\xi}{\zeta}+\frac{1}{\delta\xi}\right)K-\frac{4u^2}{3\lambda}\left\{\frac{1}{m\zeta}+\frac{1}{p\delta}\pm\frac{4w}{3m\lambda\zeta}\left[\frac{n\xi}{\zeta}+\frac{u+v}{\delta\xi}\right]\pm\frac{4w}{3p\lambda\delta}\left[\frac{q}{\delta\xi}+\frac{(u+v)\xi}{\zeta}\right]\right\}K^2,$$

$$W_{\mathrm{I}}^{c}=\frac{3m}{2}-\frac{4u(\lambda-v)}{\lambda\zeta}K-\frac{16u^2v^2}{3\lambda^3\delta\zeta}K^2,\quad W_{\mathrm{II}}^{c}=\frac{3p}{2}+\frac{4u(\lambda+v)}{\lambda\delta}K+\frac{16u^2v^2}{3\lambda^3\delta\zeta}K^2,\quad W_{\mathrm{III}}^{c}=0.$$

The meaning of the symbols is as follows:

$K=3\mathcal{C}\beta$; $\quad\zeta=3\lambda-3v-u$;
$u=-2E\overline{r^2}/7$; $\quad m=u-v-\lambda$;
$w=-2\Delta\overline{r^2}/7$; $\quad n=u+v-\lambda$;
$v=-A'/2$; $\quad p=u-v+\lambda$;
$\lambda=(u^2+\frac{2}{3}uv+v^2)^{\frac{1}{2}}$; $\quad q=u+v+\lambda$;
$\delta=3\lambda+3v+u$; $\quad\xi=p/m$.

The coefficients A and B of the rhombic field are given by the expressions $u+w=-2A\overline{r^2}/7$ and $u-w=-2B\overline{r^2}/7$.

When these expressions are incorporated in (1) we obtain the principal magnetic susceptibilities. It is found convenient to express the susceptibilities in terms of the square of the empirical effective Bohr magneton number μ_B. This is defined by the relation $\chi_q=(L\beta^2/3kT)(\mu_B{}^2)_q$, where $q=a$, b or c, corresponding to the crystallographic axis along which the magnetic field is directed.

Comparison with Experiment

The formulas for the principal susceptibilities involve three parameters, A', A and B, which can be evaluated from the observed values of the three susceptibilities at a given temperature. Actually values of the parameters are chosen to reproduce as nearly as possible both the correct magnitudes and correct temperature dependence of the susceptibilities (see Fig. 2). We thus obtain $A'=-510$ cm^{-1}, $A\overline{r^2}=108$ cm^{-1} and $B\overline{r^2}=179$ cm^{-1}. The value obtained for A', the coefficient for spin-orbit coupling, is in excellent agreement with the value 500 cm^{-1} estimated by Van Vleck and Penney[4] from spectral data. No appreciable difference would result if the value 500 cm^{-1} were used rather than 510 cm^{-1}. It is interesting that the spin-orbit coefficient can thus be indirectly calculated, say to within ten percent perhaps, by magnetic calculations.

In Fig. 2 it may be seen that the magnitude, anisotropy and temperature dependence of the magnetic susceptibilities are fairly well duplicated by the theoretical results. The slight divergence with increasing temperature which Jackson observed for the two similar susceptibilities along the a and b axes may well be due to

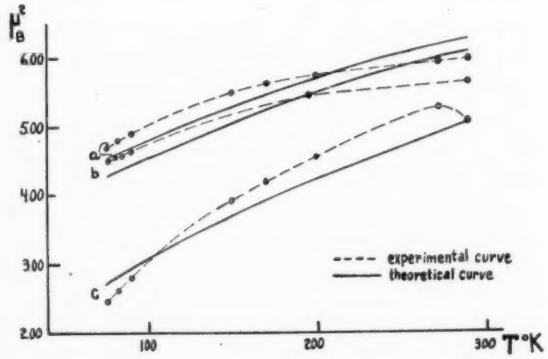

Fig. 2. Curves for the temperature variation of the square of the effective Bohr magneton number μ_B corresponding to the principal axes[11] a, b, c of $K_3Fe(CN)_6$. By definition, μ_B is connected with the susceptibility χ through the relation $\mu_B{}^2=(3kT/L\beta^2)\chi$.

crystal. Jackson's measurements show, however, that the latter system of axes, in the temperature range 75° to 290°K, is never out of coincidence with the crystallographic axes by more than a rotation by 3° about the b axis. For our purposes this small rotation may be ignored and the magnetic and crystallographic axes are taken to coincide.

variations in the force field in the crystal caused by the increasing energy of vibration. With a constant crystalline potential one would expect any magnetic anisotropy to diminish with temperature, if it changes at all, as the difference in the coefficients of the rhombic field becomes less important with respect to kT. The kink in the experimental curve for the susceptibility along the c axis probably also arises from a change in the crystalline field.

Some of the discrepancy with experiment may be due to the fact that we have neglected the matrix elements connecting $d\gamma$ and $d\epsilon$ which arise from the electrostatic energy $\sum e^2/r_{ij}$ coupling the five electrons together. Hence our calculations are not as accurate as those of Schlapp and Penney (except for their work on cobalt; cf. portion of V.V. II in fine print).[12]

Generality of Our Calculations—Conclusion

We have so far used the language of the method of crystalline potentials for the sake of convenience in presenting the procedure of calculation. However, our calculations still apply with either the method of molecular orbitals or with the use of the Slater-Pauling localized bonds.

We have spoken of the Fe^{+++} ion subject to an ionic field whereas the ion is probably much less polar in $K_3Fe(CN)_6$. Consequently, an additional perturbation not explicitly included in (3) is the spilling over of some of the CN^- electrons onto the Fe^{+++} ion, which represents a tendency toward covalent bond formation. A convenient way of treating covalent bonds is provided by the method of molecular orbitals, and is discussed more fully in V.V. II. In this method there are two types of $d\gamma$ levels, corresponding to the upper and lower roots of a secular equation which determines the proper linear combinations of the orbitals of the iron atom with the orbitals of the CN^- groups. (Cf., for instance, Fig. 2 in V.V. II.) The lower roots are bonding and, as they are each inhabited twice, do not contribute to the paramagnetic susceptibility. The upper roots are antibonding, and are so high that we consider them to be virtually uninhabited and neglect their effect. We are thus concerned only with the $d\epsilon$ orbitals. Fortunately they are nonbonding and do not combine with CN^- orbitals. Thus the covalent "spilling-over" effects do not vitiate our calculations of the magnetic susceptibility. This result is also true if we use Pauling's localized bonds instead of the method of molecular orbitals, for his $sp^3d\gamma^2$ directed bonds represent completed electron pairs which do not contribute to the susceptibility. Thus in his theory the magnetism results from the $d\epsilon^3$ orbitals, which are nonbonding and so amenable to our type of calculation.

Pauling assumed[4] that the magnetism of the $d\epsilon$ group arises entirely from the spin. Our calculation has shown that actually the orbital angular momentum of the $d\epsilon$ group contributes appreciably to the susceptibility if the field is nearly cubic. This explains why the observed susceptibility is almost twice as high as that corresponding to one free spin.[13]

In conclusion I would like to thank Professor J. H. Van Vleck for suggesting this problem and for his invaluable advice during the course of the work.

[12] In Schlapp and Penney's article, reference 6, the interelectronic energy $\Sigma e^2/r_{ij}$, which we shall call (a), is diagonalized in their unperturbed problem, but at the expense of considering the complete effect of (b) the cubic potential. They retained in Co only the part of (b) diagonal in L. We diagonalize (b) rather then (a) in the unperturbed system, since by hypothesis (b) is larger than (a) in the cyanides (unlike the sulphates). (Even at that we retain only matrix elements of (b) internal to the configuration d^5. Otherwise, the problem involves an infinite number of states and is of hopeless complexity.) Fortunately, except in Co, there are no matrix elements of (b) nondiagonal in L in the states of high spin in which Schlapp and Penney were interested (cf. fine print in V.V. II.); otherwise their accuracy would be no higher than ours.

[13] The spin-only value of μ_B is 1.73 for one free spin. The reason that Pauling did not seem to need orbital contributions to the susceptibility is that he apparently used the value $\mu_B = 2.00$ quoted by Bose, Zeits. f. Physik **65**, 677 (1930). This value is out of line with the higher values 2.3–2.4 reported by Jackson[1] and by Ishiwara, Sci. Rep. Tohoku Univ. **3**, 303 (1914); W. Biltz, Zeits. f. anorg. Chemie **170**, 161 (1928); and L. A. Welo, Phil. Mag. **6**, 481 (1928).

Symmetry Considerations Concerning the Splitting of Vibration-Rotation Levels in Polyatomic Molecules

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(Received September 30, 1935)

The interaction of rotation and vibration and perhaps other effects may split degenerate vibration-rotation energy levels of symmetrical polyatomic molecules into a number of components. The permutation symmetry of molecules containing several identical atoms provides certain restrictions on this splitting. This paper discusses the maximum number of fine-structure components, their quantum weights when nuclear spins are taken into account, and the selection rule for transitions. All arguments are based solely on symmetry considerations so that no estimate of the magnitude of the splitting is given.

DEFINITION OF COORDINATES

IN discussing the motions of the atoms in a polyatomic molecule (as distinct from the motion of the electrons) it is useful to use the Eulerian angles θ, φ, χ to describe the orientation of the molecule in space and the normal coordinates Q_1, Q_2, Q_3, $\cdots$, Q_N to describe the mutual positions of the atoms in the molecule. It is important to define these coordinates more definitely. Let the angles θ, φ, χ define a set of rotating Cartesian axes X, Y, Z, with origin at the center of gravity of the molecules. The position of any atom i can be specified by the Eulerian angles and the coordinates x, y, z relative to the rotating system. However, there are three too many coordinates so that three relations between the coordinates must be written down in order to define the rotating system uniquely. These relations are conveniently chosen to be[1a]

$$\begin{aligned} \Sigma m_i(a_i y_i - b_i x_i) &= 0, \\ \Sigma m_i(b_i z_i - c_i y_i) &= 0, \\ \Sigma m_i(c_i x_i - a_i z_i) &= 0, \end{aligned} \tag{1}$$

where a_i, b_i, c_i are the coordinates (in terms of the rotating system) of the equilibrium position of the ith atom and m_i is the mass of the atom. A transformation from the coordinates x_i, y_i, z_i to normal coordinates Q_1, Q_2, $\cdots$, Q_N can then be carried out in the usual manner and it will be found that the relations (1) are equivalent to those usually made in normal coordinate treatments; namely, that to the first approximation there is no rotational angular momentum with respect to the rotating system of coordinates.

AN APPROXIMATE WAVE EQUATION

It is natural to set up the wave equation in terms of these coordinates. This involves first expressing the kinetic energy in terms of θ, φ, χ, Q_1, Q_2, $\cdots$, Q_N and then using the result to construct the wave equation in the usual manner.[1] This is a possible, but complicated, procedure. However, if we assume that we can neglect in the classical Lagrangian expression for the kinetic energy those terms involving the normal coordinates to the first or higher powers (which means classically that we are assuming small vibrations), then the wave equation resulting from this approximate Lagrangian will be simply the sum of two parts; one the equation for the rigid rotator (coordinates θ, φ, χ), the other the equation for harmonic vibrations (coordinates Q_1, Q_2, $\cdots$, Q_N).*

The solutions of this equation are products of the type

$$\psi = R(\theta, \varphi, \chi)\, V(Q_1, \cdots, Q_N), \tag{2}$$

where $R(\theta, \varphi, \chi)$ is the rotational wave function and $V(Q_1, \cdots, Q_N)$ is the vibrational wave function.

For molecules whose equilibrium configurations possess a certain minimum symmetry; namely, at least a threefold axis of symmetry,

* Junior Fellow of the Society of Fellows.

[1a] C. Eckart, Phys. Rev. **47**, 552 (1935).

[1] B. Podolsky, Phys. Rev. **32**, 812 (1928).

* We assume here that the potential function is harmonic but this assumption does not change the final conclusions. This method of justifying the usual separation into rotational and vibrational parts does, however, depend on the choice of the rotating coordinate system defined by (1).

both the rotational and vibrational energy levels may be degenerate when the approximation considered here is used. Thus for CH_3F the functions R are the symmetrical top solutions with the energy levels

$$W_{J,K}=(h^2/8\pi^2)\{J(J+1)/A+K^2(1/C-1/A)\}, \quad (3)$$

so that levels with $|K|>0$ are doubly degenerate. For this molecule certain of the fundamental vibrational levels are also doubly degenerate so that, to this approximation, CH_3F possesses some fourfold degenerate energy levels because of its threefold symmetry axis.

It will be shown that this high degeneracy is not really required by the symmetry so that these energy levels may be split by terms which have been omitted in obtaining this simple approximation. Some degeneracy, however, will remain on account of the symmetry.

Symmetry Considerations[2]

The true energy operator, H, is unchanged by any permutation of identical particles; it is therefore invariant under the group of permutations which are equivalent to rotations of the molecule. The wave functions RV are not in general invariant under these permutations since the coordinates θ, φ, χ, Q_1, $\cdots$, Q_N, are not. Thus the permutation (123) of the three H atoms in CH_3F changes χ into $\chi+2\pi/3$ and therefore $R(\chi)$ into $e^{2\pi iK/3}R(\chi)$.

The functions RV belonging to a given approximate energy level form a *representation*[3] of the group of permutations equivalent to rotations. This representation is in general *reducible* so that by forming the correct linear combinations of these functions RV the representation can be *reduced* and each combination will correspond to one of the *irreducible representations* of the group. The technique of finding the number of wave functions with each type of symmetry has been treated in detail in a previous paper[2] and will be assumed here.

If ψ_A, ψ_B, etc., are the linear combinations of the functions RV which reduce the representation then the perturbed energy levels are determined by integrals of the type $\int\psi_A H\psi_B d\tau$. It is a consequence of group theory that if ψ_A and ψ_B belong to different irreducible representations the integral is identically zero. Therefore the energy matrix, if set up in terms of ψ_A, ψ_B, etc., will factor into diagonal blocks, the elements of each block involving only functions of one symmetry type or irreducible representation. All other elements of the matrix will vanish. Furthermore, blocks corresponding to doubly degenerate representations of the group will occur twice, so that the energy levels which are the roots of such a block of the secular equation will be doubly degenerate. Similar remarks apply to triply degenerate representations.

CH_3F as an Example

These statements may be better understood if illustrated by an example, CH_3F. From reference 2, Table X, it is found that if the rotational quantum number K has a value not divisible by three the rotational functions R for that level have the symmetry E with respect to the group of permutations equivalent to rotations. If the vibrational energy level under consideration is also doubly degenerate with the symmetry E, there will be four wave functions of the type RV, having the symmetry $E\times E=2A+E$; that is, there can be formed four independent linear combinations of the four functions RV, such that two of them are symmetrical with respect to permutations equivalent to rotations whereas the other two form a degenerate pair. Applying the theorems of the previous paragraph we obtain the energy matrix (or secular equation) shown in Fig. 1, in which only the elements in the heavy squares are different from zero and the elements of the two squares marked E are equal. As far as the symmetry is concerned, therefore, the originally fourfold level may split, under the influence of coupling terms, etc., into three levels, two of which are the roots of the quadratic equation

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[2] This paper is an extension of a previous publication (J. Chem. Phys. **3**, 276 (1935)), which considered the same symmetry questions but which obtained the total statistical weights of the unsplit energy levels. Here exactly the same methods are used, only the split levels will be considered and their separate statistical weights determined.

[3] For the meaning and use of the group theory terms employed here see E. Wigner, *Gruppentheorie* (Vieweg and Sohn); B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik* (Springer, Berlin).

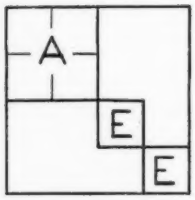

FIG. 1.

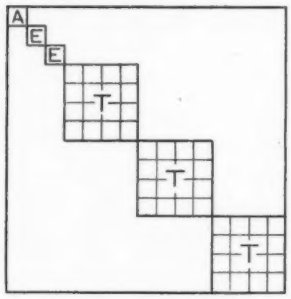

FIG. 2.

FIG. 1. Energy matrix for a sample approximate level of CH_3F. Heavy lines enclose non-zero elements.
FIG. 2. Energy matrix for a sample approximate level of CH_4.

obtained from the upper block of Fig. 1, while the remaining level is doubly degenerate and comes from either of the two equal lower blocks of the secular equation.

METHANE AS AN EXAMPLE

Methane may be similarly treated. As a sample let us consider the level with J equal to 2 and with one quantum of one of the triply degenerate vibrations excited. From Table III, reference 2 we find that the symmetry of this level is $(E+T)\times T=A+E+4T$. The secular equation for this level therefore has the form shown in Fig. 2, in which the lower three blocks are identical and the two blocks above these are identical. This energy level may therefore split into one single level (A), one double level (E), and four triple levels (T).

In connection with methane it may be pointed out that it is possible, but not proved, that even the nonvibrating rotational levels of methane may be split. For example, the level with J equal to 5 has the symmetry $E+3T$ so that in the nonvibrating state it is possible for a perturbation with tetrahedral symmetry (such as conceivably the stretching terms) to split this eleven-fold level into one double level and three triple levels. It requires further study of a more quantitative nature in order to decide whether or not such a splitting actually occurs to an appreciable degree or not. This treatment merely shows that the symmetry of the molecule does not require such a high degree of degeneracy.

SELECTION RULES

The electric moment of a molecule is a function of the coordinates of the nuclei and is unaffected by interchange of coordinates of identical nuclei. It is thus symmetrical. The integral $\int \psi_A \mu \psi_B d\tau$, determining the transition probability, is therefore zero if ψ_A and ψ_B are in different irreducible representations. The selection rule is that transitions occur only between levels of the same symmetry. This rule does not replace the ordinary selection rules but is an additional restriction.

STATISTICAL WEIGHTS OF COMPONENT LEVELS[2]

The calculation of the statistical weights of the components of a level (important for the computation of relative intensities) is carried out in exactly the same manner as in reference 2. Thus for methane the nuclear-spin functions have the symmetry $5A+E+3T$. The total wave function must have the symmetry A. Therefore the components of the sample vibration-rotation level previously discussed will have the weights shown in Fig. 3 (multiplied by $2J+1$).

MOLECULES WITH SEVERAL FRAMEWORKS

Both of the examples above are molecules possessing two "frameworks" in the sense used in reference 2. As discussed in that reference, however, this fact does not need to be taken into account in calculating the statistical weights of the levels since the total wave function must have one definite symmetry with respect to interchanges of identical particles and there will

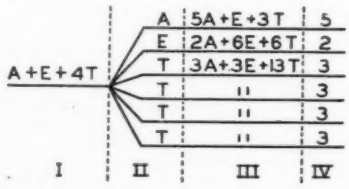

FIG. 3. Number of components, their symmetries and statistical weights (factor $2J+1$ omitted) for a sample level of methane. Regions I and II give the symmetries before and after splitting, spins not included. Region III gives the symmetries when the spin function $\psi_S(5A+E+3T)$ is included. Region IV gives the statistical weights of the components when the exclusion principle is applied (A only). The vertical order and relative spacing of the components has no significance.

be only one linear combination of the functions based on the various frameworks which will have the correct symmetry.

Conclusion

It is to be emphasized that only symmetry considerations have been used in this paper so that the results are necessarily incomplete since they do not yield any information regarding the magnitudes of the splittings to be expected. Actual energy levels may not be split to an observable extent or they may show the splitting indicated here only incompletely. It is possible also that certain of the perturbations, especially the rotation-vibration coupling, may split the approximate energy levels to such an extent that a component of one approximate level may nearly coincide with a component of another approximate level. In spite of these complications, however, the symmetry does restrict the maximum number of components which are possible and gives the selection rules and statistical weights involved. Experimental results[4] exist which may be capable of interpretation in terms of these effects but further work is necessary.

[4] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

The Molecular Structures of Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

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(Received October 7, 1935)

The structures of the molecules SO_2, CS_2, and COS have been investigated by the electron diffraction method with the following results; SO_2, $S-O=1.46\pm0.02$A; CS_2, $C-S=1.54\pm0.03$A; COS, $C-O=1.16\pm0.02$A, $C-S=1.56\pm0.03$A. The types of bond arrangement compatible with these interatomic distances are discussed. In SO_2 the molecule resonates between the structures having single-double and double-single bonds between the sulfur and the two oxygen atoms, with a bond angle of $122°\pm5°$. CS_2 is a linear molecule with the structure having the two double bonds predominating over those having a single and a triple bond. In COS the double-double bond arrangement and the structure having the triple carbon-oxygen bond predominate.

THE molecular structures of sulfur dioxide, carbon disulfide, and carbonyl sulfide have been studied by the method of electron diffraction of gases. A jet of vapor is made to intersect a beam of forty-kilovolt electrons whose diffraction pattern is registered on x-ray film. Visual measurements on the maxima and minima are correlated with those on the theoretical curves based on various molecular models. In these curves the scattering power of an atom for electrons is assumed to be constant with angle and the inelastic scattering is neglected. A detailed discussion of the procedure used in interpreting electron diffraction photographs has already been published.[1]

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† No. 501.

[1] L. Pauling and L. O. Brockway, J. Chem. Phys. **2**, 867 (1934).

Sulfur Dioxide

The sample of sulfur dioxide was redistilled from the purest commercial product.

The heavier photographs showed four maxima. The first was very strong; the second, strong and rather broad; the third and fourth were weaker but very sharp. The theoretical intensity curve, Fig. 1, is based upon a triangular model with an angle of 120° between the sulfur-oxygen bonds. No other curves are shown since the theoretical diffraction pattern is very insensitive to changes in bond angle. This effect in molecules with heavy central atoms and light outer atoms has been discussed for chlorine dioxide.[2]

The values obtained for the sulfur-oxygen distance are given in Table I. The third column

[2] L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 303, 874 (1933).

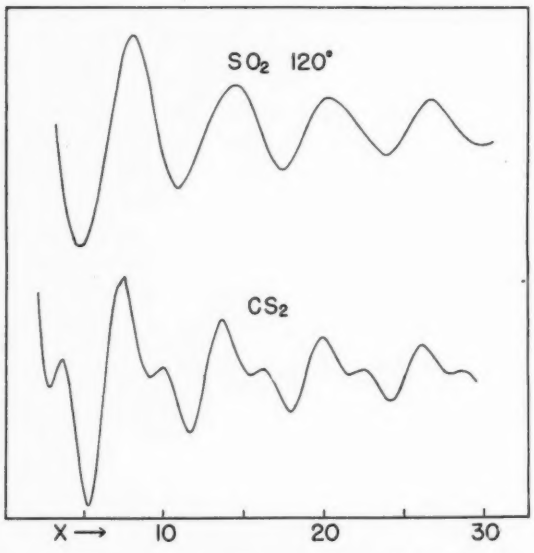


FIG. 1. Theoretical intensity curves for sulfur dioxide and carbon disulfide.

shows the observed positions of the maxima and minima, where θ is the scattering angle and λ is the wave-length associated with the electrons. The fourth column gives the positions of the maxima and minima on the theoretical curve and in the last column are listed the values of the sulfur-oxygen distance. The final value is $S-O=1.46\pm0.02$A.

An earlier electron diffraction investigation of sulfur dioxide[3] leads to the value 1.37A. This was obtained with the aid of photographs showing only one maximum and is accordingly less reliable than the present result based upon measurements of four maxima and two minima.

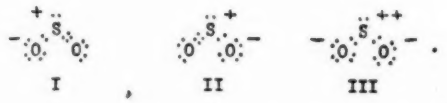
The bond angle in SO_2 has been evaluated from the studies of the vibrational spectrum in the infrared region and by the Raman technique.[4] With the aid of the fundamental frequencies ($\nu_\sigma=1361$, $\nu_\pi=1152$, $\nu_\delta=525$ cm^{-1})[5] corresponding to the three modes of vibration, the treatment of the molecule, with the two-constant "valence

TABLE I. *Sulfur dioxide.*

FOUR PHOTOGRAPHS				$\lambda=0.0606$A
Max.	Min.	$\frac{4\pi \sin\theta/2}{\lambda}$	x	
1		5.625	7.86	(1
2		9.656	14.30	
	3	11.99	17.2[illegible]	
3		13.76	20.[illegible]	1.[illegible]
	4	16.19	23.[illegible]	
4		18.15	26.[illegible]	
			Average	
$S-O=1.46\pm0.02$A				

force" potential function and the assum[illegible] that the vibration is harmonic, leads to a [illegible] of $122°\pm5°$. If this angle and the vibrat[illegible] frequencies are used in conjunction with Badger relation between the force constant interatomic distance,[6] the sulfur-oxygen separ[illegible]tion is calculated to be 1.48A, in satisfacto[illegible] agreement with our results.

The electronic structures which seem likely [illegible] contribute to the ground state of sulfur dioxid[illegible] are as follows:



A structure can be written having single bonds and only three electron pairs on one of the oxygen atoms; but this is less likely than the third of the structures above because of the greater electron affinity of oxygen. In view of the theoretical possibility of placing five electron pairs on the sulfur atom, structures may be considered having two double bonds or a single and a triple bond, but these undoubtedly make very small contributions.

The observed bond distance is 0.05A less than the sum of the covalent radii[7] for double bonds. The double bond distance required by resonance between I and II above would be shortened by the polar character of the bonds. The inclusion of III in the resonating structures would not affect the distances but this structure is probably involved because of the tendency of sulfur to assume the double plus charge as in the sulfates and thionates.

[3] R. Wierl, Ann. d. Physik **8**, 544 (1931).
[4] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **A137**, 605 (1933); **A138**, 531 (1932). See also A. Jonescu, Comptes rendus **196**, 1476 (1933); **197**, 35 (1933); and J. H. Clements, Phys. Rev. **47**, 224 (1935). We have not considered Jonescu's structure because of the incomplete nature of the rotational analysis upon which it is based, and the dependence upon Wierl's erroneous value of the S—O distance.
[5] R. M. Badger and L. G. Bonner, Phys. Rev. **43**, 305 (1933).
[6] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).
[7] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

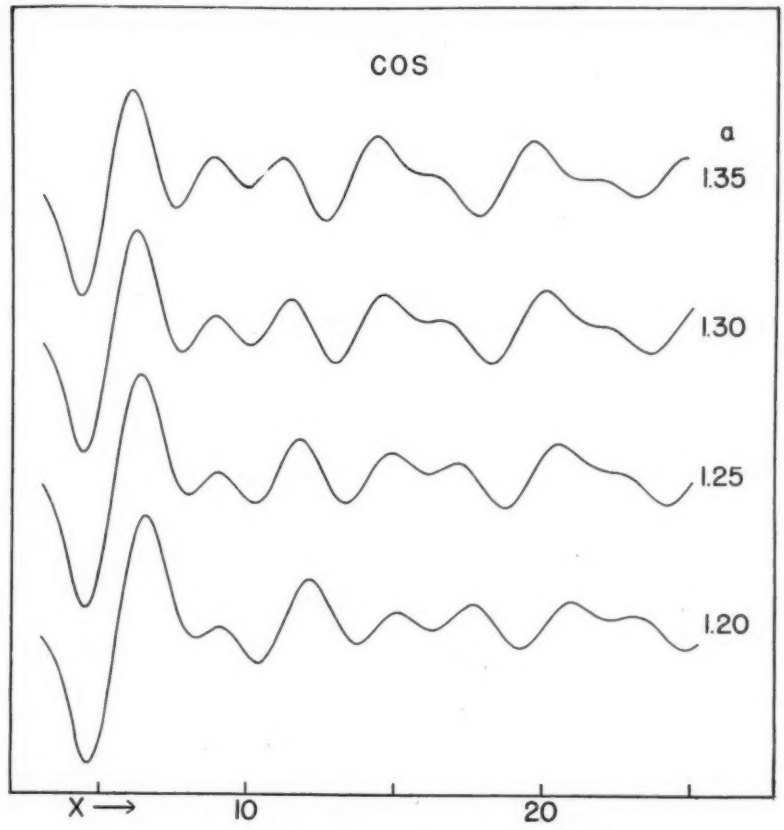


FIG. 2. Theoretical intensity curves for carbonyl sulfide.

The angle is determined by the separate electronic structures and the value determined spectroscopically is just that to be expected between a single and a double bond on a tetrahedral atom.

TABLE II. *Carbon disulfide.*

Eight Photographs			$\lambda = 0.0607$A	
Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	x	a
1		4.713	7.25	1.538
1a		6.312	9.85	1.560
	2	7.623	11.52	1.512
2		8.698	13.55	1.559
2a		10.63	16.10	1.515
	3	11.63	17.84	1.535
3		12.65	19.84	1.568
3a		14.58	22.40	1.536
	4	15.54	24.12	1.553
4		16.81	26.12	1.554
			Average	1.543

C−S=1.54±0.03A

CARBON DISULFIDE

The carbon disulfide photographs were characterized by four strong maxima each followed by a weak maximum and a deep minimum. This appearance, which is also observed in the theoretical curve corresponding to a linear model (Fig. 1), is due to the fact that one of the two different interatomic distances in the molecule is just twice the other. The results given in Table II lead to a carbon-sulfur distance of 1.54±0.03A in essential agreement with Wierl's value[3] of 1.58A.

The electronic structures to be considered are the three having the double-double, the single-triple and the triple-single arrangement of bonds. If the three were of nearly equal importance the triple bond distance should be observed as in the analogous case of carbon dioxide. The table of radii gives 1.63A for the double bond and 1.43A for the triple bond. Observations on the

TABLE III. *Carbonyl sulfide.*

FIVE PHOTOGRAPHS Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	$x_{1.35}$	$x_{1.30}$	$a_{1.35}$	$a_{1.30}$
				$\lambda = 0.0602$A		
1		5.23	6.05	6.18	1.156	1.181
	2	6.41	7.51	7.75	1.171	1.209
2		7.67	8.80	8.90	1.147	1.160
	3	8.70	9.95	10.10	1.144	1.161
3		9.82	11.15	11.45	1.135	1.165
	4	10.93	12.60	12.90	1.153	1.180
4		12.20	14.30	14.60	1.172	1.196
	5	13.33		15.90		1.193
5		14.04	16.15	16.60	1.151	1.182
	6	15.31	17.80	18.20	1.162	1.189
6		16.65	19.60	20.10	1.177	1.206
				Average	1.157	1.184
				(Ave. Dev.	0.011	0.013)
			C−O = 1.16±0.02A			
			C−S = 1.56±0.03A			

spectroscopic molecules P_2 and PN[8] indicate that the ratio of triple to single bond radius for elements in the second row of the periodic table should be larger than the value 0.79 used in the radius table. From $r_0 = 1.86$A in P≡P the triple bond radius for phosphorus is 0.93A. Adding to this the triple bond radius for nitrogen (0.55A) we get 1.48A in agreement with the observed value for P≡N of 1.49A. Accordingly with the value 0.93A for the triple bond radius of phosphorus the triple-single bond radius ratio becomes 0.846 for second row elements. Applying this ratio to sulfur and adding the triple bond radius of carbon we obtain 1.49A for the predicted value of the carbon-sulfur triple bond.

The observed value 1.54A is 0.05A larger than the triple bond distance; therefore the contribution of the second and third structures above is considerably less important than that of the first. This conclusion is supported by the very small tendency of second row elements to form triple bonds; in fact, the two compounds of phosphorus mentioned in the preceding paragraph are the only known examples, and they exist only in an electrical discharge.

[8] G. Herzberg, Ann. d. Physik **15**, 677 (1932); J. Curry, L. Herzberg and G. Herzberg, Zeits. f. Physik **86**, 348 (1933).

CARBONYL SULFIDE

Theoretical curves were calculated for four linear models of carbonyl sulfide corresponding to different ratios (a values in Fig. 2) of the carbon-sulfur to carbon-oxygen distances. That the second ring was observed to be very nearly as strong as the third and the maximum beyond the fourth was scarcely more than a shelf fixes the ratio of the two distances at about 1.34. Table III includes the calculations for the two models with ratios of 1.35 and 1.30. The final values are C−O = 1.16±0.02A and C−S = 1.56 ±0.03A.

Dornte[9] obtained electron diffraction photographs of carbonyl sulfide and reported calculations of the theoretical scattering for only one model (corresponding to a distance ratio of 1.40). This ratio and the distance which he reports (C−O = 1.13±0.05A, C−S = 1.58±0.08A) differ from ours by less than the uncertainty which he ascribes to his measurements.

The value observed for the carbon-sulfur separation is essentially the same as that in the CS_2 molecule while the carbon-oxygen distance agrees with the value 1.15A in carbon dioxide and with the triple bond radius sum 1.13A. The foregoing discussion of the character of the carbon-sulfur bond applies also to the case of carbonyl sulfide.

We are grateful to Professor Linus Pauling for suggestions and criticisms.

[9] R. Dornte, J. Am. Chem. Soc. **55**, 4126 (1933).

Thermodynamic Properties of Sulfur Compounds

II. Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

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(Received October 7, 1935)

The thermodynamic properties of sulfur dioxide, carbon disulfide, and carbonyl sulfide are calculated from the molecular constants obtained by electron diffraction and Raman and infrared spectra. $-(F^0-E_0^0)/T_{298.1}=50.95$, 48.28, 47.39; $S^0_{298.1}=59.40$, 56.84, 55.34 for SO_2, $CS_2(g)$, and COS, respectively. The results are applied to several reactions involving these compounds. The free energies of formation of $CS_2(l)$ and COS at 298.1°K are +15.24 and −40.48 kg.cal.

THE results of the preceding paper[1] give the following values for terms which appear in the approximate equations for the entropy and free energy functions such as given by Kassel:[2]

SO_2, $\frac{1}{2}R\ln I_AI_BI_C=-262.93$, $R\ln\mu=-1.377$,
CS_2, $R\ln I=-172.03$, $R\ln\mu=-1.377$,
COS, $R\ln I=-173.23$, $R\ln\mu=0$.

The vibration frequencies were taken as follows:

SO_2, 1361, 1152, 525,[3]
CS_2, 1523, 655.5, 396.8 (2),[4]
COS, 2079, 859, 527 (2).[5]

Because of the lack of adequate data to determine the anharmonic factors, the molecules were treated as harmonic oscillators and the vibrational contributions determined from the tables of Gordon and Barnes.[6] This also ignores the Fermi interaction, but the errors introduced are not serious for work of the accuracy intended herein.

The results shown in Table I were obtained from the equations;

$$SO_2,\quad (F^0-E_0^0)/T=-4R\ln T-5.49+[(F^0-E_0^0)/T]_{\text{vib.}},$$
$$S^0=4R\ln T+13.44+S_{\text{vib.}},$$
$$C_p^0=7.946+C_{\text{vib.}};$$
$$CS_2,\quad (F^0-E_0^0)/T=-(7/2)R\ln T-7.93+[(F^0-E_0^0)/T]_{\text{vib.}},$$
$$S^0=(7/2)R\ln T+14.88+S_{\text{vib.}},$$
$$C_p^0=6.954+C_{\text{vib.}};$$
$$COS,\quad (F^0-E_0^0)/T=-(7/2)R\ln T-7.40+[(F^0-E_0^0)/T]_{\text{vib.}},$$
$$S^0=(7/2)R\ln T+14.35+S_{\text{vib.}},$$
$$C_p^0=6.954+C_{\text{vib.}}.$$

The values for SO_2 are probably accurate to within 0.15 unit, while those for CS_2 and COS should be within 0.1 unit of the true values.

SULFUR DIOXIDE

A similar calculation for SO_2 has recently been made by Gordon,[7] who applied his results to the reactions

$$\tfrac{1}{2}S_2+O_2=SO_2, \qquad (1)$$

$$SO+\tfrac{1}{2}O_2=SO_2, \qquad (2)$$

$$SO_2+3H_2{}^8=H_2S^9+2H_2O,{}^{10} \qquad (3)$$

$$2CO_2{}^{11}+\tfrac{1}{2}S_2{}^{12}=SO_2+2CO.{}^{13} \qquad (4)$$

(References are to the sources of $(F^0-E_0^0)/T$ values.) Since the new values of $-(F^0-E_0^0)/T$ are 0.38 larger than Gordon's, the values of log K_1 and log K_2 in Gordon's Table I should be in-

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* National Research Fellow in Chemistry, 1933–35. Now at Stanford.
† No. 502.
[1] P. C. Cross and L. O. Brockway, J. Chem. Phys. **3**, 821 (1935).
[2] L. Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).
[3] R. M. Badger and L. G. Bonner, Phys. Rev. **43**, 305 (1933).
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[7] A. R. Gordon, J. Chem. Phys. **3**, 336 (1935).
[8] W. F. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[9] P. C. Cross, J. Chem. Phys. **3**, 168 (1935).
[10] A. R. Gordon, J. Chem. Phys. **1**, 308 (1933).
[11] L. Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).
[12] C. W. Montgomery and L. Kassel, J. Chem. Phys. **2**, 417 (1934). Corrected by Cross, reference 9.
[13] J. O. Clayton and W. F. Giauque, J. Am. Chem. Soc. **55**, 5071 (1933).

TABLE I. *Free energy, entropy, and heat capacity of SO_2, CS_2, and COS.*

T	$-(F^0-E_0^0)/T$			S^0			C_p^0		
	SO_2	$CS_2(g)$	COS	SO_2	$CS_2(g)$	COS	SO_2	$CS_2(g)$	COS
298.1	50.95	48.28	47.39	59.40	56.84	55.34	9.51	10.91	9.92
400	53.49	50.90	49.81	62.32	60.19	58.41	10.35	11.85	10.95
500	55.50	53.04	51.79	64.72	62.91	60.93	11.08	12.52	11.66
600	57.21	54.89	53.50	66.79	65.24	63.11	11.67	13.00	12.21
700	58.71	56.51	55.01	68.62	67.27	65.03	12.11	13.37	12.64
800	60.05	57.97	56.37	70.26	69.08	66.74	12.44	13.65	12.98
900	61.27	59.30	57.61	71.74	70.70	68.28	12.70	13.86	13.26
1000	62.39	60.51	58.75	73.09	72.16	69.69	12.90	14.02	13.49
1100	63.42	61.63	59.81	74.33	73.50	70.98	13.05	14.15	13.68
1200	64.37	62.67	60.79	75.47	74.74	72.18	13.17	14.26	13.84
1300	65.27	63.65	61.71	76.53	75.89	73.30	13.27	14.35	13.97
1400	66.11	64.57	62.58	77.52	76.96	74.34	13.35	14.42	14.08
1500	66.91	65.44	63.40	78.44	77.97	75.31	13.42	14.48	14.17
1600	67.66	66.25	64.17	79.30	78.91	76.22	13.47	14.53	14.25
1700	68.37	67.02	64.90	80.12	79.79	77.09	13.52	14.57	14.32
1800	69.04	67.75	65.60	80.90	80.61	77.91	13.56	14.61	14.38

TABLE II.

Eq.	Reactions	ΔE_0^0	$\Delta F^0/T=-R\ln K$				
			$T=298.1$	400	600	900	1500
(3)	$3H_2+SO_2=H_2S+2H_2O$	−47.98	−152.2	−109.7	−67.5	−38.5	−14.5
(4)	$2CO_2+\frac{1}{2}S_2=2CO+SO_2$	47.65	139.0	97.2	56.5	29.4	8.1
(5)	$CO_2+H_2S=COS+H_2O$	7.0	23.7	17.6	11.5	7.4	4.3
(6)	$COS+H_2S=CS_2+H_2O$	8.4	31.3	23.9	16.7	11.8	8.0
(17)	$CO+\frac{1}{2}S_2=COS$	−22.2	−57.9	−38.3	−19.1	−6.4	−3.6
(18)	$2COS=CO_2+CS_2$	1.4	7.6	6.4	5.2	4.4	3.8
(19)	$CS_2=C(\text{graph})+S_2$	3.6	12.6	9.7	6.9	5.2	3.8

creased by 0.08. By using the values of ΔE_0^0 suggested by Gordon, several values of $\Delta F^0/T=-R\ln K$ have been calculated for reactions (3) and (4) and given in Table II. Comparisons with experimental results are found in Table III.

CARBON DISULFIDE AND CARBONYL SULFIDE

Since the thermal measurements on these compounds are known to be subject to some errors, values of ΔE_0^0 were obtained from equilibrium measurements. The results of Terres and Weseman[14] on the reactions

$$CO_2+H_2S=COS+H_2O,\quad \Delta E_0^0=7.0\text{ kg. cal.} \tag{5}$$

and

$$COS+H_2S=CS_2+H_2O,\quad \Delta E_0^0=8.4 \tag{6}$$

gave exceptionally consistent results having no pronounced trend with temperature.

From the reactions

$$H_2+\tfrac{1}{2}S_2=H_2S,\quad \Delta E_0^0=-19.6,^{9} \tag{7}$$

$$H_2+\tfrac{1}{2}O_2=H_2O,\quad \Delta E_0^0=-57.1,^{10} \tag{8}$$

$$2S=S_2,\quad \Delta E_0^0=-102.6,^{15} \tag{9}$$

$$2O=O_2,\quad \Delta E_0^0=-117.3,^{16} \tag{10}$$

one obtains

$$E_0^0(H_2O)-E_0^0(H_2S)=-44.9. \tag{11}$$

Combining with the results on reactions (5) and (6) gives

$$E_0^0(COS)-E_0^0(CO_2)=51.9, \tag{12}$$

$$E_0^0(CS_2)-E_0^0(COS)=53.3 \tag{13}$$

Since

$$E_0^0(CO)-E_0^0(CO_2)=125.4,^{11} \tag{14}$$

$$E_0^0(CO)-E_0^0(CS_2)=20.2, \tag{15}$$

[14] E. Terres and H. Weseman, Zeits. f. angew. Chemie **45**, 795 (1932).

[15] A. Christy and S. M. Naudé, Phys. Rev. **37**, 903 (1931).

[16] B. Lewis and G. von Elbe, J. Am. Chem. Soc. **57**, 612 (1935).

TABLE III.

Eq.	T	$-R \ln K$ Calc.	Obs.	Ref.	Calc.-Obs.
(3)	1160	−25.1	−27.1	18	+2.0
	1362	−18.2	−19.8	18	+1.6
	1473	−15.2	−16.2	18	+1.0
	1645	−11.2	−11.7	18	+0.5
(4)	1275	13.7	16.3	19	−2.6
	1460	8.9	10.9	19	−2.0
(5)	623	11.2	11.3	14	−0.1
	673	10.3	10.3	14	0
	723	9.5	9.5	14	0
	773	8.8	8.8	14	0
	823	8.2	8.2	14	0
	873	7.7	7.5	14	+0.2
(6)	973	11.1	11.3	14	−0.2
	1023	10.7	11.0	14	−0.3
	1073	10.3	10.3	14	0
	1123	9.9	9.7	14	+0.2
	1173	9.6	9.0	14	+0.6
(17)	533	23.9	22.5	20	+1.4
	575	20.7	19.1	20	+1.6
	1073	2.3	2.2	21	+0.1
	1223	−0.2	−1.4	21	+1.2
(18)	533	5.5	8.2	22	−2.7
	575	5.3	9.4	22	−4.1
	573	5.3	5.3	21	0
	673	4.9	4.9	21	0
	753	4.7	3.7	21	+1.0

$$E_0^0(\mathrm{CO}) \quad -E_0^0(\mathrm{COS}) = 73.5. \qquad (16)$$

These results are expressed as differences inasmuch as there still seems to be some doubt as to the absolute values of E_0^0 for carbon compounds.

The E_0^0 differences given here have been applied to the reactions

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{S_2} = \mathrm{COS}, \qquad \Delta E_0^0 = -22.2, \quad (17)$$

$$2\mathrm{COS} = \mathrm{CO_2} + \mathrm{CS_2}, \qquad \Delta E_0^0 = 1.4, \quad (18)$$

$$\mathrm{CS_2} = \mathrm{C(graphite)}^{17} + \mathrm{S_2}, \quad \Delta E_0^0 = 3.6. \quad (19)$$

The reaction

$$\mathrm{CO} = \mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2}, \quad \Delta E_0^0 = 27.4^{17} \quad (20)$$

was also employed to obtain ΔE_0^0 for reaction (19). The results are summarized in Tables II and III.

[17] J. O. Clayton and W. F. Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

The comparisons on reactions (17) and (18) are satisfactory considering that the values of Lewis and Lacey on (18) are admittedly only approximate. The large discrepancies between observed and calculated results for (19) have been discussed by Randall.[23] The experimental measurements are in such poor agreement with each other that it seems justified to consider the indirectly calculated values as the most reliable so far available. The experimental results are not given here because this reaction will be considered more fully in a forthcoming paper by Professor Randall.

The free energies of formation of CS_2 and COS may be obtained from these results as follows:

$$\mathrm{C(graphite)}^{17} + \mathrm{S_2}^{12} = \mathrm{CS_2(g)}, \quad \Delta F_{298.1} = -3.75,$$

$$2\mathrm{S(rh)} = \mathrm{S_2}, \qquad \Delta F_{298.1} = +19.44,^{7}$$

$$\mathrm{CS_2(g)} = \mathrm{CS_2(l)}, \quad \Delta F_{298.1} = -0.45,^{24}$$

$$\mathrm{C(graphite)} + 2\mathrm{S(rh)} = \mathrm{CS_2(l)}, \quad \Delta F_{298.1} = +15.24.$$

The value obtained from a rather uncertain value of the heat of combustion of CS_2 is 17.15.[24]

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2}^{25} \quad \Delta F_{298.1} = -50.20,$$
$$+ \tfrac{1}{2}\mathrm{S_2} = \mathrm{COS_2}$$
$$\mathrm{S(rh)} = \tfrac{1}{2}\mathrm{S_2}, \qquad \Delta F_{298.1} = 9.72,$$

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2} \quad \Delta F_{298.1} = -40.48.$$
$$+ \mathrm{S(rh)} = \mathrm{COS},$$

This value is in essential agreement with the thermal value of −39.80.[24]

[18] M. Randall and F. R. Bichowsky, J. Am. Chem. Soc. **40**, 368 (1918).
[19] J. B. Ferguson, J. Chem. Soc. **40**, 1626, 1900 (1918).
[20] Lewis and Randall, *Thermodynamics* (1923), p. 581. Recalculated with Gordon's value for the free energy of formation of S_2, reference 7.
[21] A. Stock, W. Siecke and E. Pohland, Ber. **57**, 719 (1924).
[22] G. N. Lewis and W. N. Lacey, J. Am. Chem. Soc. **37**, 1976 (1915).
[23] Randall, Am. Chem. Soc. San Francisco, August, 1935.
[24] Parks and Huffman, *Free Energies of Some Organic Compounds* (1932), pp. 204–206.
[25] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **55**, 172 (1933).

The Molecular Structure of Nickel Carbonyl

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(Received October 7, 1935)

Electron diffraction by the vapor of $Ni(CO)_4$ leads to a molecular model in which the four carbonyl groups have a tetrahedral arrangement about the nickel atom with the distances $Ni-C=1.82\pm0.03$A and $C-O=1.15$A. These distances are compatible with resonance between two electronic structures in which the C—O bond resonates between triple and double electron pair bonds and the Ni—C bond between single and double electron pair bonds. Nickel carbonyl is the first quadricovalent compound of neutral nickel whose structure has been determined, and its tetrahedral configuration is contrasted with the square arrangement of bonds in the quadricovalent compounds of divalent nickel ion.

THE molecular structure of nickel carbonyl and its relation to the more general problem of the orientation of the four bonds in quadricovalent nickel compounds has interested chemists for more than ten years. In 1926 Blanchard and Gilliland[1] gave a detailed discussion of the chemical properties of nickel carbonyl and deduced an electronic structure which was intended to be compatible with these properties and at the same time would allow for a complete shell of eighteen electrons around the nickel atom. It is interesting to note that their suggestion that four electrons are shared between each carbon and the nickel atom is equivalent in the modern concept of valence to double electron pair bonds between the carbon and nickel atoms, to which we shall resort in order to account for our observations.

In 1930 Sugden[2] proposed a cyclic structure for nickel carbonyl in which the nickel and the four carbon atoms form a five-membered ring with an oxygen atom attached to each carbon.

Pauling[3] predicted from a theoretical consideration of the relative strengths of bonds formed by *s*, *p*, and *d* eigenfunctions that in the compounds of divalent nickel ion in which four covalent bonds are attached to the nickel atom the four bonds should be directed toward the corners of a square. In support of this prediction he cited the isomorphism of $K_2Ni(CN)_4\cdot H_2O$ with the corresponding palladium compound and the known[4] square arrangement of the bonds in the chloropalladites and chloroplatinites. Because of later misinterpretations it should be pointed out that the same theoretical considerations suggest a tetrahedral arrangement when four bonds are formed with neutral nickel, as in the case of nickel carbonyl.

Sugden[5] found further evidence in favor of the square arrangement in quadricovalent nickelous compounds in the preparation of interconvertible isomers of the nickel derivatives of methyl benzyl-, methyl *n*-propyl-, and methyl *n*-butyl glyoxime. These were explained as cis- and trans-isomers, which could not exist with a tetrahedral arrangement of the four bonds. A similar relation was found much earlier by Tschugaeff[6] for the nickel derivatives of monoethylglyoxime but he made no attempt to explain this isomerism. Additional crystallographic evidence is found in the isomorphism[7] of $BaNi(CN)_4\cdot 4H_2O$ and $BaPt(CN)_4\cdot 4H_2O$. Even more conclusive is the recent work of Cox, Pinkard, Wardlaw and Webster[8] on the nickelous derivative of salicylaldoxime in which two molecules of the aldoxime are joined by four bonds to the nickel atom. Oscillation and rotation x-ray photographs show that the crystal belongs to the space group $P2_1/m-C_{2h}^5$. With two molecules in the unit cell (as determined from the dimen-

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** Contribution No. 503.

[1] A. A. Blanchard and W. L. Gilliland, J. Am. Chem. Soc. **48**, 872 (1926).

[2] S. Sugden, *The Parachor and Valency* (Albert Knopf, New York, 1930), p. 189.

[3] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); **54**, 988 (1932).

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[5] S. Sugden, J. Chem. Soc. **1932**, 246. H. Covell and S. Sugden, ibid. **1935**, 621.

[6] Tschugaeff, J. Russ. Phys. Chem. Soc. **42**, 1466 (1910).

[7] H. Brasseur, A. de Rassenfosse and J. Pierard, Zeits. f. Krist. **88**, 210 (1934). H. Brasseur and A. de Rassenfosse, Mem. Soc. Sci. Liége. [3] **18**, 1 (1933).

[8] E. G. Cox, F. W. Pinkard, W. Wardlaw and K. C. Webster, J. Chem. Soc. **1935**, 459.

sions of the unit and the density) the molecule is required to have a center of symmetry. This is possible only if the molecule is planar with a trans-configuration of the two salicylaldoxime groups. Robertson[9] has similarly investigated the nickel derivative of phthalocyanine and found that the molecule has a center of symmetry, which requires a planar configuration of the four bonds to the nickel atom.

For the case of nickel carbonyl the zero electric moment observed by Sutton and Bentley[10] indicates that the molecule must have either the square or tetrahedral configuration (with the carbonyl groups collinear with the nickel-carbon bonds) as opposed to a cyclic arrangement. These authors favored the tetrahedral configuration on the basis of Pauling's prediction.

The Raman and ultraviolet absorption spectra of nickel carbonyl have been studied by Dadieu and Schneider,[11] Anderson,[12] Thompson and Garratt,[13] and Duncan and Murray.[14] The first two investigators pointed out that the almost identical frequency of vibration of the carbonyl groups in nickel carbonyl and the carbon monoxide molecule is strong evidence for an identical structure of the carbon-oxygen bond in the two cases. Duncan and Murray investigated both the Raman and ultraviolet absorption spectra as well as the vibrations of a mechanical model of a square planar molecule. They ascribe incorrectly to Pauling a prediction of the square configuration for nickel carbonyl. From the fair agreement between their assignment of the frequencies in the spectra and the frequencies observed in the model and from a calculation of the symmetry number they conclude that the plane square model is correct or at least more probable than the tetrahedron. Wilson[15] points out that the failure of Duncan and Murray to observe the selection rules in assigning the observed frequencies to modes of vibration of the molecule has led to an incorrect assignment of the frequencies; hence, their conclusions are invalidated.

Laird and Smith[16] have recently redetermined the parachor value of nickel carbonyl but reached no conclusion concerning the configuration of the four bonds.

The present investigation was undertaken in the hope of obtaining decisive evidence on the structure of nickel carbonyl and determining the values of the interatomic distances, which would be useful in considering the types of bonds involved.

The sample of nickel carbonyl was obtained from the Eastman Kodak Company. This was vacuum distilled and pumped off while frozen with liquid air in order to remove carbon monoxide. The small residue of nickel hydroxide produced by hydrolysis was left behind in the distillation. The compound was photographed with the sample at room temperature with a diffraction point to film distance of 10.43 cm and with the use of electrons having a wavelength of 0.0606A.

The photographs show eight maxima with a characteristic appearance of the diffraction pattern. The first maximum is weak while the second and third are both very strong and very sharp. The fourth maximum is weak and lies close to the third while the minimum following is broad and well defined. The fifth maximum is strong and sharp with the sixth, seventh, and eighth rings falling off in intensity in regular order.

Quantitative estimates were made of the apparent intensities of the successive rings and these data were combined with the observed values of the function $(4\pi \sin \theta/2)/\lambda$ to obtain an atomic distribution curve in the manner described by Pauling and Brockway.[17] This curve, reproduced in Fig. 1, represents the average distribution of scattering power around the atoms in the molecule of nickel carbonyl. Since the electrons in the beam are scattered chiefly by their interaction with the atomic nuclei the positions of the maxima in the distribution curve represent internuclear distances in the

[9] J. M. Robertson, J. Chem. Soc. **1935**, 615.
[10] L. E. Sutton and J. B. Bentley, Nature **130**, 314 (1932). L. E. Sutton, R. G. A. New and B. Bentley, J. Chem. Soc. **1933**, 652.
[11] Dadieu and Schneider, Anz. Acad. Wiss. Wien, Math. Naturwiss. Klasse **68**, 191 (1931).
[12] J. S. Anderson, Nature **130**, 1002 (1932).
[13] H. W. Thompson and A. P. Garratt, J. Chem. Soc. **1934**, 524.
[14] B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[15] E. B. Wilson, Jr., J. Chem. Phys. **3**, 59 (1935).
[16] F. W. Laird and M. A. Smith, J. Am. Chem. Soc. **57**, 266 (1935).
[17] L. Pauling and L. O. Brockway, J. Am. Chem. Soc., in proof.

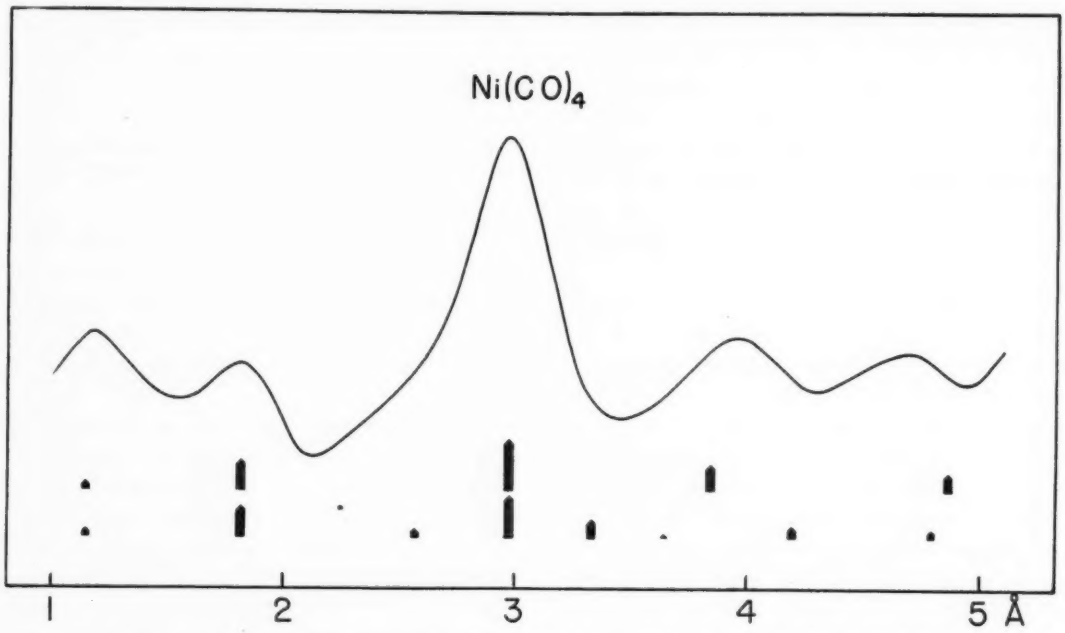


FIG. 1. Curve showing the observed radial distribution of scattering power in $Ni(CO)_4$. The two rows of arrows show the distances in the tetrahedral (upper) and square (lower) models based on the observed Ni−C and C−O distances.

molecule. Accordingly without any assumptions about the structure of the molecule we know that it must contain atomic separations near the values 1.18A, 1.82A, 2.97A, and 3.96A. This result may be combined with the usual procedure[18] for interpreting electron diffraction photographs in the consideration of square and tetrahedral arrangements of the atoms in nickel carbonyl.

The molecular models for which calculations of the theoretical intensity of electron scattering were made are alike in having four carbonyl groups joined to a central nickel atom with the line joining the carbon and oxygen atoms in the respective carbonyl groups passing through the central atom. This restriction is reasonable on the basis of a triple bonded carbon monoxide joined by a single bond to the nickel atom. Models were included in which the oxygen atoms are attached to the nickel as well as those having carbon atoms adjacent to the nickel atom. In the square configuration the carbonyl groups are directed toward the corners of a square; in the tetrahedral arrangement they point to the vertices of a regular tetrahedron. Calculations were made for each of these arrangements with the ratio of carbon-oxygen to nickel-carbon distances varying from 0.55 to 0.65. Five of these curves are shown in Fig. 2 in which the intensity of elastically scattered electrons (calculated with atomic scattering powers which are constant over the scattering angle) is plotted against $(4\pi \sin \theta/2)/\lambda$ with an assumed Ni−C separation of 2.00A to fix the horizontal scale.

The general qualitative appearance of the photographs is well reproduced by the tetrahedral curves in Fig. 2. The square models with a C−O/Ni−C ratio of 0.625 or greater are unsatisfactory because they would require the seventh maximum to be appreciably stronger than the sixth and they fail to show the subsidiary fourth maximum following the strong third maximum. For values of the ratio below 0.625 the fourth maximum appears at a position about halfway between the third and fifth whereas the fourth is observed on the photographs to be much closer to the third maximum.

The quantitative comparison is given in Table I. The first column of data is calculated from the measured ring diameters and the wave-length

[18] L. Pauling and L. O. Brockway, J. Chem. Phys. 2, 867 (1934).

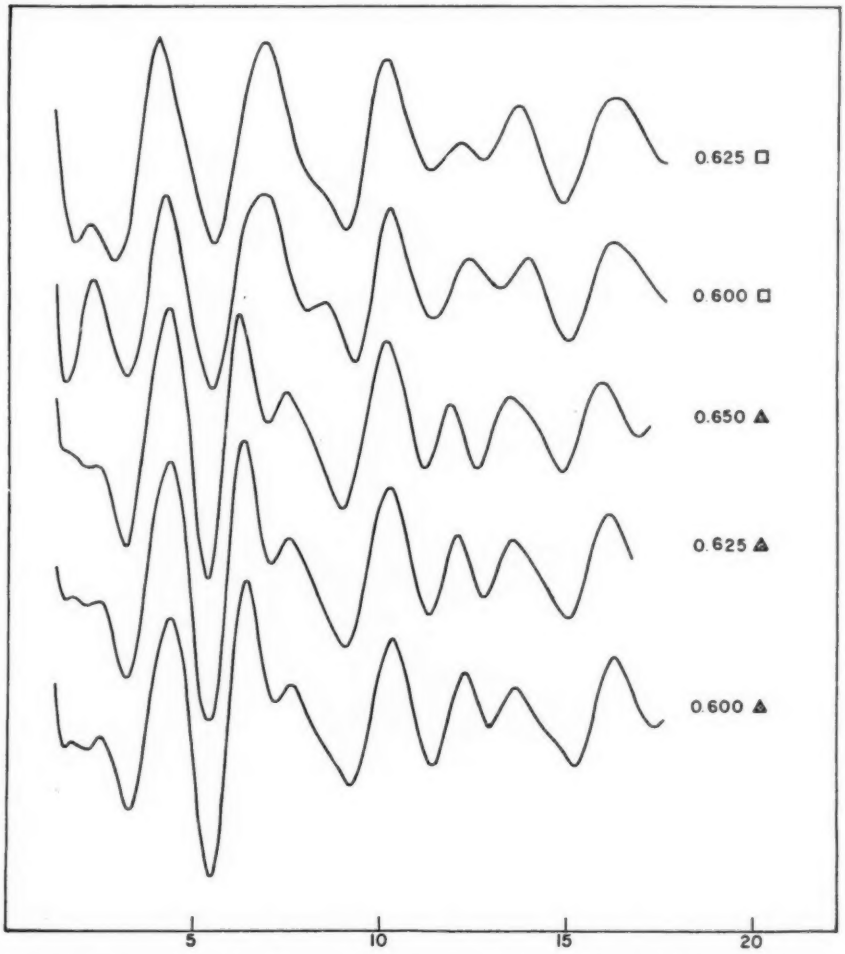


FIG. 2. Theoretical intensity of electron scattering by $Ni(CO)_4$ with constant atomic scattering factors. The upper two curves correspond to square models and the lower three to tetrahedral models.

used. The second represents the visually estimated intensities used for the atomic distribution curve. The next five columns give the values of the indicated points on the theoretical curves, while the last five columns show the corresponding values for the size of the molecule in terms of the assumed distances. The assumed nickel-carbon separation of 2.00A is multiplied by the **a** values to give the experimentally determined values of the Ni−C distance. The C−O distance is then determined by means of the ratios used in the respective models.

The square models in the table are definitely inferior to the tetrahedral ones since they show an average deviation in the values for the size of the molecule more than three times as great as that for the tetrahedral models. An even more serious discrepancy is found in the deviation of the value calculated from the fourth maximum. This maximum is subject to the St. John effect,[19] in which the apparent position of an unsymmetric ring is shifted in the direction of the greater contrast. In this case the effect would lead to too low a value of the molecular size. It will be observed in the tetrahedral models that the value from the fourth maximum is around five percent below the average from other rings whereas in the only square model

[19] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. **56**, 2374 (1934).

TABLE I.

Max.	Min.	$\frac{4\pi \sin\theta/2}{\lambda}$	Intensity	Tetrahedral $x_{0.650}$	Tetrahedral $x_{0.625}$	Tetrahedral $x_{0.600}$	Square $x_{0.625}$	Square $x_{0.600}$	Tetrahedral $a_{0.650}$	Tetrahedral $a_{0.625}$	Tetrahedral $a_{0.600}$	Square $a_{0.625}$	Square $a_{0.600}$
1		2.63	5										
2		4.86	10	4.30	4.32	4.34	4.05	4.18	0.885	0.889	0.893	0.833	0.860
	3	5.92		5.35	5.38	5.43	5.50	5.45	.904	.909	.917	.929	.921
3		6.92	10	6.23	6.30	6.38	6.87	6.80	.901	.911	.922	.993	.983
	4	7.74		6.96	7.05	7.15		8.00	.900	.911	.924		1.034
4		8.70	6	7.45	7.55	7.60		8.45	(.856)	(.868)	(.874)		.972
	5	9.96		8.97	9.05	9.20	9.03	9.27	.900	.908	.924	.906	.931
5		11.09	7	10.12	10.25	10.35	10.10	10.20	.913	.924	.934	.911	.920
	6	12.14		11.20	11.30	11.40	11.35	11.38	.923	.931	.939	.935	.938
6		13.17	3	11.86	12.08	12.25	12.10	12.32	.901	.918	.930	.919	.936
	7	14.08		12.58	12.77	12.92	12.74	13.15	.894	.907	.918	.904	.934
7		15.01	2	13.45	13.58	13.64	13.65	13.83	.896	.904	.908	.909	.921
	8	16.25		14.85	15.05	15.20	14.85	15.00	.914	.926	.936	.914	.923
8		17.38	2	15.90	16.12	16.25	16.25	16.22	.915	.928	.935	.935	.934
								Average	.904	.914	.924	.917	.939
								Ave. Dev.	.007	.007	.007	.023	.027
				Final Value Ni−C = 1.82 ±0.03A				Ni−C	1.808	1.828	1.848		
				C−O = 1.15 ±0.02A				C−O	1.175	1.142	1.109		
				Tetrahedral arrangement of atoms									

which shows the fourth ring at all the value is four percent too high. Since the deviation is in the wrong direction it can be ascribed only to the unsatisfactory character of the square model.

Among the tetrahedral models we eliminate those having a ratio below 0.625 since they give values for the C−O distance lower than that observed in carbon monoxide. Since carbon monoxide is observed to have the triple bond distance, there is no form of covalent bond which could exist between the carbon and oxygen atoms in nickel carbonyl which would have a smaller interatomic distance. The effect on the triple bond itself of forming the extra bond to the nickel atom could scarcely be that of strengthening the bond and shortening the distance. Accordingly, we take the observed distance in carbon monoxide, 1.14A, as the lower limit for the carbon-oxygen separation in nickel carbonyl.

An upper limit on the C−O/Ni−C ratio may be placed at 0.65 since in models above that value of the ratio, some of the qualitative intensity comparisons occur in the wrong direction (such as seventh maximum greater than sixth). Accordingly we choose as most probable the tetrahedral model with a ratio of 0.63 and having Ni−C = 1.82 ±0.03A and C−O = 1.15 ±0.02A.

Inspection of the atomic distribution curve now leads to its interpretation in the light of the foregoing result. The vertical arrows in Fig. 1 show all of the interatomic distances in a tetrahedral and a square molecule, respectively, of nickel carbonyl which has the Ni−C and C−O distances given above. The height of the arrows is proportional to the products of the scattering powers of the respective pairs of atoms. The large, sharp maximum at 2.97A corresponds to the Ni−O and the C−C distances which coincide in the tetrahedral model. The hump at 1.82A is the Ni−C separation. The less reliable hump for C−O appears at 1.18A but it should be observed that the difference between Ni−O and Ni−C is just 1.15A.

The atomic distribution curve also corroborates our choice of the tetrahedral arrangement. In the experience of Pauling and Brockway[17] the three distances in the square model at 2.57A, 2.97A, and 3.33A would not combine to give the sharp maximum observed at 2.97A.

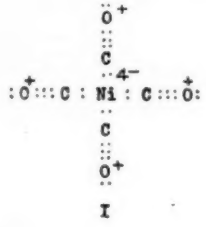
Two practically independent methods of treating the electron diffraction photographs thus lead to the conclusion that nickel carbonyl is a tetrahedral molecule with the dimensions given above.

DISCUSSION

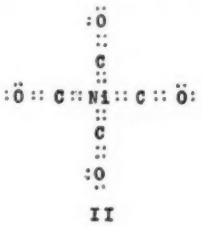
The observed carbon-oxygen distance, 1.15A, agrees with the value for carbon monoxide molecule and thus supports the previous evidence for a similarity of bonding in the carbonyl group in this compound and carbon monoxide. Since the latter compound is known[20] to resonate

[20] L. Pauling, J. Am. Chem. Soc. **54**, 1000 (1932).

between the double bond and triple bond structures the question of finding this same state in nickel carbonyl is raised. With a triple bond between carbon and oxygen only a single electron pair bond could be formed between nickel and carbon as indicated in the first of the following structures. The formal charges are obtained by



I



II

dividing the electrons in the bond and they indicate the directions of the semipolar bonds (sometimes represented by arrows). The nickel-carbon distance is observed to be 0.18A smaller than the sum of the covalent single bond radii. It is improbable that the nickel radius is in error by this amount or that the single bond would be shortened that much by its semipolar character (in spite of the rather large negative charge on the nickel atom); accordingly, it is suggested that this shortening is produced by resonance with the structure II in which all of the bonds are represented as double electron pair bonds. This represents an extreme state since the four bonds would perhaps not assume this character all at the same time. The double bonds are formed by placing two unshared pairs on oxygen and bringing one of the unshared pairs of $3d$ electrons on nickel into the nickel-carbon bond. Since both the electrons and eigenfunctions are available, nickel does not share with the elements of the first row in the periodic table the restriction to four electron pair bonds. Structure II gives each atom a zero formal charge. Resonance between I and II explains the observed shortening of the nickel-carbon bond and allows the carbon-oxygen bond to exhibit a similar resonance between the double and triple states which it shows in carbon monoxide. For each of the bonds in nickel carbonyl the stronger of the resonating components determines the distance.

The directional properties[3] of structure I are determined by the fact that all five of the $3d$ eigenfunctions of neutral nickel are probably occupied by unshared pairs and the $4s$ and three $4p$ functions used in forming the four single bonds have the usual tetrahedral arrangement. For structure II no prediction can be made since the problem of four double bonds formed from d^4sp^3 has never been studied. Since structure I probably predominates in the resonance it is likely that its directional properties determine those of the normal state of the molecule; but in fact the observed tetrahedral configuration cannot be used as a criterion for the proposed resonance. It should again be noted that although this is the first definitely tetrahedral configuration observed in quadricovalent nickel compounds all of the other substances studied have been compounds of divalent nickel ion.

We are deeply grateful to Professor Linus Pauling for many suggestions and criticisms.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

The Conductance of Salt Crystals

Recently Jost[1] has derived an expression for the conductance of salt crystals by postulating in detail the exact mechanism involved in the transport of ions through the crystal. The expression obtained by Jost does not appear adequate to account for the conductance behavior of various salts throughout the whole range of temperature, and if it can be shown that the same form of expression could be obtained by very general considerations, then it would appear that the mechanism postulated by Jost is not necessarily the correct one.

We find it possible to obtain the Jost equation by assuming that when an ion becomes activated it moves a certain average distance $\bar{x}$ before it loses its mobility. The number of ions activated per cubic centimeter per second, is given by the expression originally used by one of the authors[2] in the theory of unimolecular reactions $\nu n_0 e^{-Q/RT}$. Here ν is the frequency of the ion vibration in the lattice, n_0 is the number of ions per cubic centimeter, and Q may be identified with $E/2+U$ in Jost's formula. The diffusion coefficient D is then given by the expression $\frac{1}{2}\bar{x}^2\nu e^{-Q/RT}$, and when reasonable numerical values are introduced the value obtained for D is within the same order of magnitude as Jost's value.

It is not assumed that the conductance of salt crystals can be described completely in terms of expressions as simple as the one given above, but we do believe that any *reasonable* mechanism that may be postulated will lead to essentially the same type of formula.

W. H. RODEBUSH
T. G. COOKE

[1] Jost, J. Chem. Phys. **1**, 466 (1933).
[2] Rodebush, J. Am. Chem. Soc. **45**, 606 (1923); J. Chem. Phys. **1**, 440 (1933).

Vibrations of Benzene and Raman Spectra of Benzene-d and Benzene-d_2

In Table I we give the preliminary results of measurements, which we were performing on benzene-d and p-benzene-d_2, while Wood[1] published Raman frequencies of benzene-d_6. Experimental error cannot account for the increase from 2270 (C_6H_5D) to 2279 ($C_6H_4D_2$). Several lines of p-benzene-d_2 are more diffuse than the corresponding lines of benzene-d, indicating perhaps an equilibrium between the three isomers of benzene-d_2.

TABLE I.

C_6H_6	C_6H_5D	p-$C_6H_4D_2$	C_6H_6	C_6H_5D	p-$C_6H_4D_2$
3059 cm^{-1}	3059 cm^{-1}	3053 cm^{-1}	— cm^{-1}	1007 cm^{-1}	1008 cm^{-1}
3047	2270	2279	991	980	979
1606	1593	1587	849	851	848
1584	1571	1565	—	—	638?
1174	1176	1176	606	602	602

TABLE II.

D	i	$\prod_i \nu_i(D)/\prod_i \nu_i(C_6H_6)$ exp. (according to Wilson)	exp. (with ν_9 = 1178, ν_{10} = 849)	calc. (ref. 2)
p-$C_6H_4D_2$	1, 2, 6, 7, 8, 9	0.723	0.725	0.7075
	10	1.002	0.999	1.0000
C_6D_6	1, 2	0.715	0.715	0.7075
	6, 7, 8, 9	0.541	0.514	0.5005
	10	0.741	0.780	0.7761

Applying a relation between the frequencies of isotope molecules, previously derived and proved in the case of deuterochloroform,[2] to Wood's results and to our own, we can test Wilson's[3] correlations of the benzene frequencies to the vibrations. The discrepancies between experimental and calculated values indicate, that not all correlations can be correct. (See Table II.) Indeed, the exchange of the correlations of frequencies 9 and 10 yields satisfying agreement. The agreement yields a confirmation of Wood's correlations of frequencies 1, 2, 6, 7, 8 and 8.

We have begun with measurements on other isotopes of benzene. Dr. Ph. Gross, Vienna, to whom the authors are indebted for directing their attention to the preparation of the two benzenes, will shortly report on measurements of the vapor pressures.

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W. STRICKS

Technische Hochschule,
Institut für physikalische Chemie,
Vienna,
October 25, 1935.

[1] R. W. Wood, J. Chem. Phys. **3**, 444 (1935).
[2] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[3] E. B. Wilson, Jr., Phys. Rev. **46**, 146 (1934); cf. also ibid. **45**, 706 (1934).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 3 NUMBER 12

DECEMBER, 1935

Published by the
AMERICAN INSTITUTE OF PHYSICS
Incorporated
LANCASTER, PA., AND NEW YORK, N. Y.

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LANCASTER PRESS INC., LANCASTER, PA.